ORGANIC CHEMISTRY

For Intermediate Students

BY

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PREFACE

The present work is based on the lecture notes on a systematic course of Organic Chemistry culled through an experience of presenting it to Intermediate classes, extending over two decades. The taxt herein is intended to cover the syllabuses prescribed for the Intermediate Examinations of the Indian Universities and Education Boards.

The methods of presentation has certain special feature enumerated below, which will very much simplify the mastery of the subjects, and will at the same time lay a solid foundation in its essentials, that will be helpful in creating in the student a real incentive for study of the subject in higher stages.

The special features claimed for this book are

1. Giving in detail the molecular structure of the carbon compounds and the various connected reactions by means of their representation with a mechanical devise calculated to impart a systematic and clear grasp of the subject.
2. Discussing in detail the general methods of preparation, as also the general properties of the various families followed by their application in the study of typical members.
3. Presentation of seventeen tables intended to give a connected summary of the various compounds.
4. The essentials of the subject matter of a chapter are emphasised by variations in type in order to facilitate speedy recapitulation on the part of the student.

Inspite of all the care that was taken in bringing out the book, it is apprehended that errors and omis-

sions might have escaped observation, as its publication had to be hurried through. Communications concerning such lapses will be gratefully received.

It is my pleasant duty to record my grateful thanks for all the help received in bringing out this book. I am particularly indebted to Dr. B. B. Malvea, Principal, E. C. College, Allahabad for the trouble he took in going through most of the manuscrip. as also for his healthy criticism and invaluable advice.

JALPA PRASAD.

CONTENTS

INTRODUCTION.

Up to the end of the eighteenth century Organic Chemistry was believed to be that branch of chemistry which dealt with substances produced in bodies of living (plants and animals) under the influence of the *Vital Force* supposed to be associated with all living organisms. The earlier chemists were unable to prepare artificially substances, like sugar, vegetable oils, gums, resins, rubber, dyes, urea and other products of animals and plants in their laboratories. They, therefore, were compelled to conclude that the *Vital Force* was necessary for their production. Such substances were, therefore, classified as organic compounds. Organic Chemistry was hence defined as that branch of chemistry which dealt with these and similar other substances.

In the year 1828 Friedrich Wohler, the famous German chemist, however, succeeded in preparing urea [a white and crystalline solid, originally occurring in the urine of animals] in his laboratory simply by heating ammonium cyanate, (a substance purely inorganic in origin), quite independently of the agency of the "Vital Force".

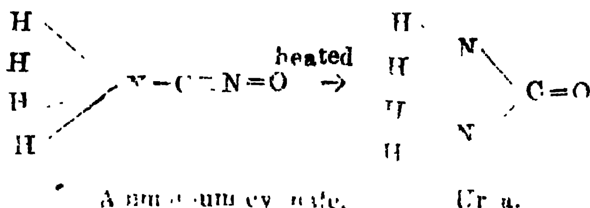


FRIEDRICH WÖHLER.

The Famous German Chemist whose work on getting Urea from Ammonium Cyanate overthrew the "Vital Force" theory in 1828.

Reaction in Wöhler's experiments expressed graphically.

Note:—In graphic representations the valency of all elements present in a molecule of a compound is shown by the number of bonds or dots attached to it.



Ammonium cyanate. Urea.

From the above graphic representations of the two compounds, we find that in the conversion of ammonium cyanate into urea, there is nothing added to or subtracted from the molecule of ammonium cyanate; yet it is changed into a compound, due to only the readjustment of the atoms in the molecule itself.

During this chemical change we observe that

(1). the oxygen atom, which was linked with the atom of nitrogen in ammonium cyanate, gets attached to the carbon atom in the molecule of urea, and

(2). the nitrogen atom which is pentavalent in ammonium cyanate becomes trivalent in the molecule of urea.

Such a chemical change, resulting in the conversion of one substance into another, only by the readjustment of the atoms within a molecule, is called *Intramolecular reaction*. Wohler, thus, pointed out that when ammonium cyanate is heated, it undergoes *Intramolecular change* and is converted into a new compound urea, which has the same percentage composition as ammonium cyanate, but which has altogether different chemical and physical properties. Such compounds—having the same percentage compo-

sition, but different chemical and physical properties—are commonly met with in the study of Organic Chemistry. The difference in the chemical and physical properties of such compounds, is due to the different arrangements of atoms in the molecules. This phenomenon is called **Isomerism** and the compounds involved therein are known as **Isomers** of one another. Ammonium cyanate and urea are thus the isomers of each other.

Organic compounds.

Wohler's work on the synthesis of urea was soon followed by the synthesis of numerous compounds like alcohol, vinegar, resins, rubber, dyes and camphor in the laboratory from simple inorganic substances, quite independently of the *Vital Force.* This undermined the faith of chemists in the theory of the *Vital Force.* and today thousands of compounds, previously considered to be products only of the living organisms, can easily by synthesised without the influence of the Vital Force. Hence, there is left no line of demarcation between organic and inorganic compounds based on the theory of *Vital Force.*

Though the terms "Organic" and "Inorganic" are still retained in the chemical world, the basis of this classification is entirely different today. Organic compounds today are the compounds, which have carbon as the main constituent element and **Organic Chemistry therefore is the chemistry of carbon compounds.** The simple carbon compounds however, like *carbon monoxide, carbon dioxide, and carbonates,* are usually studied as inorganic compounds and they will therefore not be considered in this book.

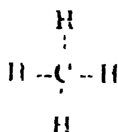
Since, Organic Chemistry is a special branch of chemistry which deals with the compounds, having carbon element as an essential constituent; it will be useful to mention at this stage the following three important characteristic properties of carbon :—

(1). The carbon atom is uniformly tetravalent, and all its four valencies are apt to be equally active.

(2). The carbon element can link with itself in a remarkable way, giving rise to a series of stable compounds of *many* carbon atoms.

(3). The carbon element forms compounds ordinarily with only a few other elements such as halogen, oxygen, nitrogen and sulphur. The compounds of carbon and hydrogen—are known as hydrocarbons and they are the most important substances as they constitute the parent of other carbon compounds. Since, the valency of carbon atom is four and that of the hydrogen is one, the simplest hydrocarbon, having all the valencies of carbon atom satisfied, will have the molecular formula CH_4. This parent hydrocarbon is methane more popularly known as marsh gas.

The graphic formula of methane is

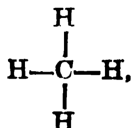


The carbon element, as has already been pointed out has a strong linking capacity with other carbon atoms. We can thus have 2, 3, 4, 5, 6 and even more carbon atoms linked one with the other, either in an open chain or in a closed chain system leading to two broad classifications of organic compounds, namely (1) Open chain or the Aliphatic (2) Closed chain or Aromatic compounds.

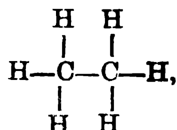
Open chain or Aliphatic Hydrocarbons.

The following are some of the Open chain hydrocarbons along with their graphic formulae :—

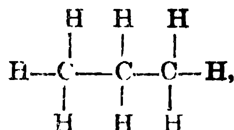
(1). **Methane**



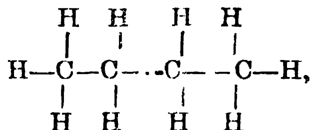
(2). **Ethane**



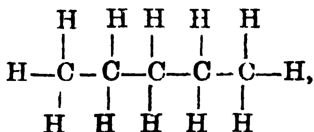
(3). **Propane**



(4). **Butane**

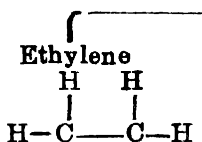


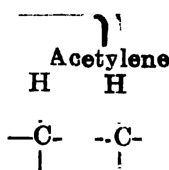
(5). **Pentane**



The above mentioned five hydrocarbons are the compounds in which each of the four bonds of every carbon atom is fully satisfied, and hence, they are all saturated hydrocarbons. On the other hand, when one or more than one of the carbon atoms present in a molecule are not fully satisfied, the compounds are known as unsaturated.

Example of unsaturated hydrocarbons



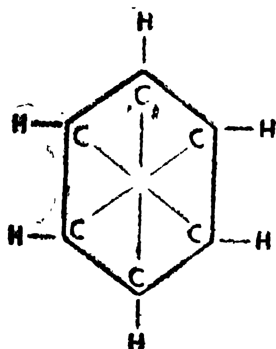


(1) **Ethylene**	(2) **Acetylene**
It is an example of the unsaturated hydrocarbon in which only one bond of each of the two adjacent carbon atoms is free. These two free bonds join together to give a double linkage between the two adjacent carbon atoms. Ethylene is thus graphically represented as follows :—	It is an example of the unsaturated hydrocarbon in which each of the two adjacent carbon atoms has two free bonds. These bonds join together to give a triple linkage between the two adjacent carbon atoms. Acetylene is thus graphically represented as follows :—
H H | | H—C=C—H Ethylene	H H | | C≡C Acetylene

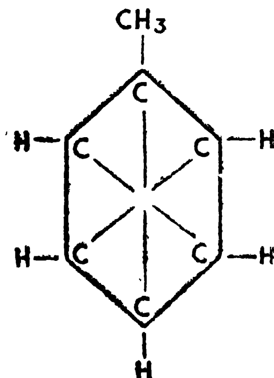
Closed Chain or Aromatic Hydrocarbons.

The following are some of the closed chain hydrocarbons along with their graphic formulæ :—

(1). **Beneze.**



(2). **Toluene.**



As a result of the strong linking capacity of carbon atoms, there is a profusion of carbon compounds. We are today familiar with hundreds of organic compounds. It is interesting to note that although carbon combines relatively with only a few elements like hydrogen, halogen, oxygen, nitrogen and sulphur, yet organic compounds are classified into well defined **Families**. Each family consists of various members, which are chemically similar and whose molecular formulæ are found in arithmetical progression with a common difference of CH_2, forming what is khown as the homologous series.

CHAPTER I.

Purification, Qualitative and Quantitative Analysis of Organic Compounds.

Before giving a systematic account of organic chemistry, it is necessary to describe some of the simple processes, used in the purification of organic compounds, as they have to be obtained in a pure form for the study of their composition and properties, We shall describe the methods used in their purification of solids and liquids :—

Purification of solid compounds.

There are three processes :—

(1) Crystallisation,

(2) Fractional crystallisation.

(3) Sublimation.

Notes:—(1) Each of these processes is to be repeated till the desired degree of purity is achieved.

(2) The purity of an organic solid is tested by its sharp and constant melting point, the determination of which is described subsequently on page 12.

The above three processes are described one after another :—

1. Crystallisation.

(*a*) The purification of an organic solid mixed with inorganic substances.

The mixture is shaked or warmed with alcohol, chloroform, ether or some other suitable organic

solvent, in which the substance to be purified is soluble. The insoluble substances can then be separated by filtration described below :—

Filtration.

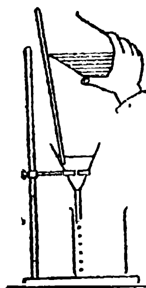


Fig 1

It is a process to separate the suspended solid particles or precipitates from a liquid. The arrangement of the apparatus for this process is shown in the Fig. 1. In this process of filtration, the filter paper should be fitted into the funnel in such a way as to remove all air spaces between the filter paper and the glass surface, otherwise the process of filtration is retarded.

Filter paper folding and fitting :—

The filter paper is folded once along its diameter, next along its radius slightly oblique, so as to make it a cone. Put the right hand thumb into the cone and press it down into the funnel Put in a little water into the filter cone now and continue pressing gently the inner fold of the filter paper till the funnel makes one or two complete round, eliminating all the air bubbles from the entire surface.

Filter paper fitting.

The filter paper is fitted into the funnel as shown below :—



Fig. 2.

After filtration. the filtrate is concentrated to a point suitable for crystallisation, then it is allowed to stand till the crystallisation is ocmplete. The crystals of the solute are separated by filtration and they are dried. The process is repeated till the desired degree of purity is attained.

(2) Fractional Crystallisation.

(*b*) The purification of an Organic solid mixed with other organic substance.

Dissolve the mixture in a solvent, in which one of the components is more soluble than the other. The crystals separated earlier from such a solution, will be mostly the solute, which is less soluble in the solvent selected The crystals of such a solute are separated by filtration. The filtrate is next concentrated and cooled. The crystals separating out now, will be mostly the solute whose solubility in the solvent is greater. Subjecting both the crops of crystals so obtained, to the similar process of crystallisation several times, the components of the mixture can be separated and obtained in a high degree of purity. *The process of repeated crystallisation and separation into two or more crops of crystals is known as fractional crystallisation.* This process is very useful in industrial works.

3. Sublimation.

(*c*) The Purification of a mixture of a volatile solid with a non-volatile substance.

The mixture is heated in a dish covered over by another basin, which is kept cool. This basin should be fairly deep and is placed inverted over the dish containing the mixture.

The volatile compound. sublimates on the inner surface of the covering basin.

Testing the purity of a solid.

A pure organic solid should give a sharp and constant melting point

Determination of Melting Point.

Select a capillary tube A as shown in figure 3. Take a small quant ty of the dry and powdered substance at the open and wider end of the tube A. Tap it down, till the solid reaches right up to the sealed end of the tube shown in B, Attach the tube to the stem of an accurate thermometer with a rubber band. Take care that the sealed end of the tube, containing the solid, is at the level of the bulb of the thermometer as shown in C.

Suspend the thermometer now into the beaker, containing a stirrer and a clear liquid, whose boiling point is higher than the melting point of the solid under examination. Keep the rubber band clear of the liquid bath as shown in D. The liquid is heated over a low flame and is kept well stirred, till the substance taken in the capillary tube melts. The temperature at which the substance begins to melt is quickly noted. If the solid substance is pure it will give a sharp and a constant melting point, otherwise, the process o purification is to be repeated.

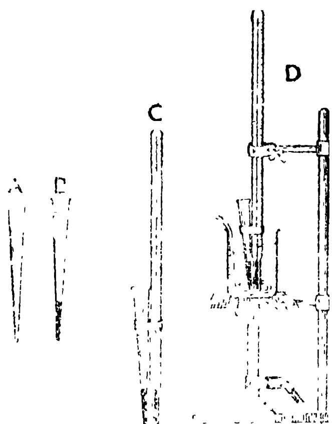


Fig. 3

Purification of a Liquid.

There are four processes :—

(1) Distillation.
(2) Fractional distillation.
(3) Distillation under reduced pressure.
(4) Steam distillation.

Notes :—(1) Each of these processes is to be repeated, till the desired degree of purity is achieved.

(2) The purity of an organic liquid is tested by the sharp and constant boiling point, the determination of which is described on page 18. The above four processes are described one after another.

(1) Distillation

(a) Purification of an organic liquid dissolved in another liquid when the Boiling Points of both the liquids are fairly far apart.

The mixture is heated in a distilling flask F. fitted up with a thermometer T, the bulb of which is kept a little below the side tube, which is connected with a condenser C and a receiver R, as shown in the Fig 4.

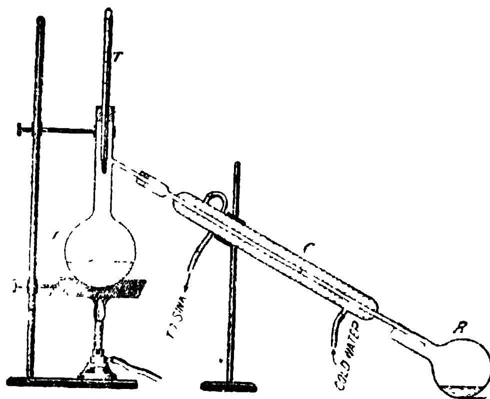


Fig. 4.

The liquid having a lower boiling point distills over first and is collected in the receiver R. which is not changed so long as the temperature remains constant. As the temperature begins to rise and reaches the boiling point of the other liquid, the distillate is collected in another receiver, so long as the temperature remains constant at the boiling point of the liquid having higher boiling point.

(2) Fractional Distillation.

(b) Purification of an organic liquid dissolved in another liquid, when the boiling point of the two liquids are not far apart.

During the distillation of such a mixture, the temperature rises continuously and the complete separation of the constituents of the mixture, is possible only by *fractional distillation*, in which the distillate, is collect in different receivers at the interval of 5° to 10° as needed. The contents of the different receivers are, redistilled in the same manner over and over again, till the constituents of the mixture are obtained in pure condition.

To make this process of fractional distillation more efficient and convenient, the flask A is fitted with a fractionating column F provided with a thermometer T, as shown in the figure 5. [Several types of fractionating colums are in use].

The vapours of the mixture, while ascending the fractionating column F are cooled and the vapour of the less volatile liquid condenses more and more, as it goes up through a series of obstructions, and is returned back into the distilling flask. Thus the vapour issuing forth from the top of the fractionating column, contains a high percentage of the vapour of the

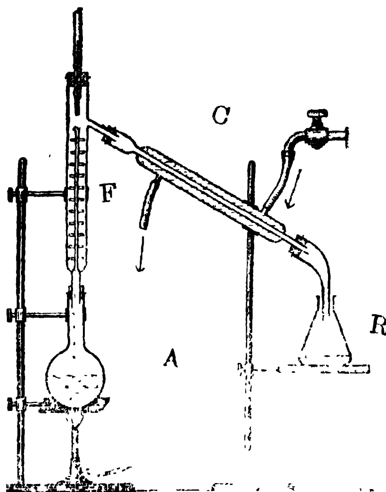


Fig. 5.

more valatile liquid. This distillate collected in the receiver is very rich in the liquid, which is more volatile. Subjecting these products of fractional distillation to the same operation twice or thrice, the different constituents of the mixture, are obtained in a pure condition. Repeated distillation, are thus avoided with the use of a fractionating column.

(3) Distillation under Reduced pressure.

(c) Purification of a liquid dissolved in another, when the components of the solution are such as are decomposed before or at their Boiling Point.

In such cases, the distillation or even fractional distillation has to be done under reduced pressure, knowing as we do, that liquids can be made to boil at a low temperature at reduced pressure. For distilling a liquid, undecomposed under reduced pressure, the

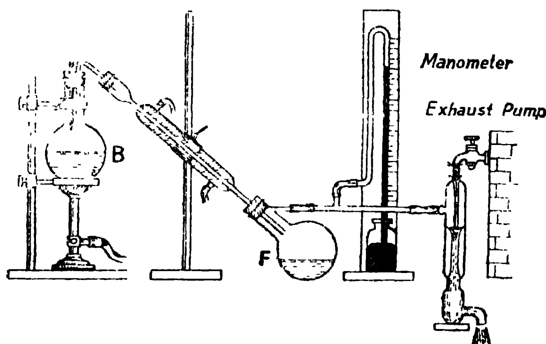


Fig. 6.

receiver F used in the arrangement is a distilling flask, the neck of which is connected to the condenser air-tight. The side tube of the receiver is attached air tight to an exhaust pump, as well as to a monometer

through a T-tube, as shown in figure 6. Thus, as the exhaust pump works, the liquid is made to boil, under reduced pressure at a lower temperature, at which it distills over undecomposed.

(4) Steam Distillation.

(d) Separation of a liquid from another when one of the components of the mixture is Volatile in Steam.

The arrangement used for the purpose of *steam distillation* is shown in figure 7.

The mixture is taken in the flask inclined as shown in the diagram. A rapid current of steam generated in a vessel D. is bubbled through the liquid in flask F. The steam and the vapour of the

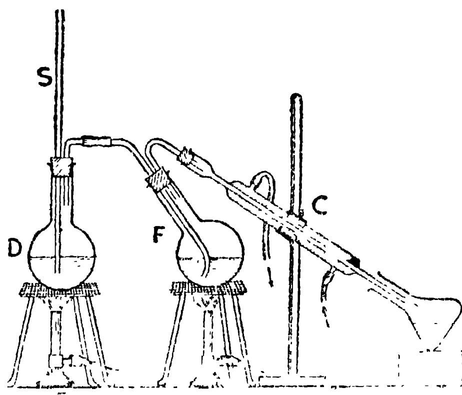


Fig. 7.

volatile substance in the mixture are condensed in the condenser C and collected in the receiver. The organic liquid in the receiver, if soluble in water, is separated by *distillation* ; but if it is immisable, the liquid is separated with a *separating funnel.*

Use of a Separating Funnel.

The mixture is taken in a *separating funnel* as shown in figure 8, The mixture is allowed to stand for sometime, during which, the mixture separates out in two definite layers. the heavier liquid being at the bottom. Now open the stop cock carefully and run out the lower portion in a separate vessel.

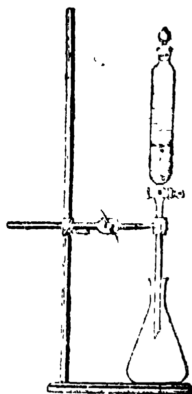


Fig. 8.

Testing the purity of a Liquid

A pure organic liquid should always give a sharp and a constant boiling point, if the atmospheric pressure remains unchanged during the experiment.

Determination of Boiling Point.

Select a fine capillary tube A, sealed at one end and open at the other, as shown in figure 9. Put this capillary tube into an ignition tube B, keeping the seal.d end of the capillary tube up. The liquid under examination is introduced into the ignition tub , just enough, as to completely cover the top of the capillary tube. Next the tube is attached to the stem of the thermometer with a rubber band as shown

in D. Suspend the thermometer now into the beaker containing a stirrer and a clear liquid whose B. P. is

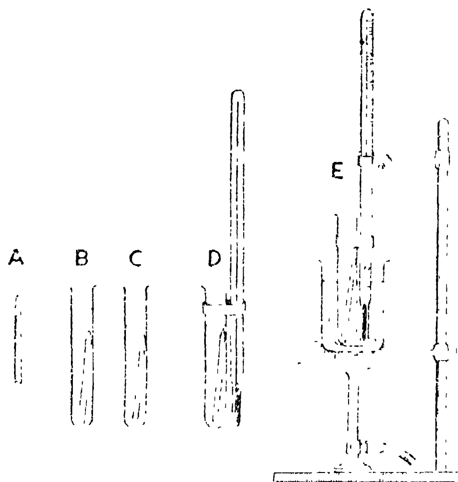


Fig. 9.

higher than the B. P. of the liquid under examination. The liquid is heated over a low flame and is kept well stirred. Watch carefully the lower end of the capillary tube. You would notice that a stray bubble comes out of the capillary tube from its open end directed towards the bottom of the ignition tube. You are now very close to the boiling point of the liquid. Continue to watch carefully and you would notice another bubble followed by more; but soon after a regular stream of bubbles will issue forth and *just and the moment*, note the reading on the thermometer. This is the boiling point of the liquid. This may be checked by repeating the experiment twice or thrice.

Qualitative Analysis.

Detection of Nitrogen, Sulphur and the Halogen in an organic substance or a mixture.

Take a piece of sodium cut to the size of a pea. Press it between a few folds of a blotting paper, so as to remove completely, traces of kerosene oil from surface of the sodium piece. Introduce it into an ignition-tube which is a very small and narrow tube of glass. Next, introduce into it a pinch of the substance finely powdered. Hold the ignition tube with a paper-holder or better in an asbestos pad and warm the tube gently, moving it in and out of the flame for sometime. If the substance under examination is *a liquid*, a longer ignition tube should be used; and the warming should be continued longer and more cautiously, so that the liquid is not volatilized before it is able to act on the sodium piece. Next, heat it strongly for about 10 to 15 minutes till all apparent reactions have ceased; and the bottom of the tube shows signs of melting. Now cool and crush it carefully in a small basin containing not more than 10 c.c. of water. Boil it and filter. Collect the filtrate in a test-tube and divide the filtrate into 4 parts :—

1. Use part A for the detection of nitrogen.
2. Use part B for the detection of sulphur.
3. Use part C for the detection of bromine and iodine.
4. Use part D for the detection of chlorine only.

1. Treatment of Part A.

Add to it a few drops of NaOH solution and a saturated solution of ferrous sulphate little by little till ferrous hydroxide is completely precipitated. Boil it and cool under tap-water. Now add only a few drops of ferric chloride. Shake and add to it conc : HCl till the precipitate, formed earlier dissolves completely. If there appears a blue precipitate or even a green solution, the presence of nitrogen is confirmed, otherwise, it is absent.

2. Treatment of part B.

Add to it a drop or two of a freshly prepared sodium-nitro-prusside solution. If there is a violet colouration, the presence of sulphur is confirmed, otherwise, it is absent.

3. Treatment of part C.

Add to it a strong solution of chlorine water in excess and a little chloroform. Shake it well. If the chloroform at the bottom of the test tube appears :—

(*i*) brown——bromine is confirmed.
(*ii*) violet——iodine is confirmed.
(*iii*) colourless—bromine and iodine are absent.

4, Treatment of part D for chlorine only.

(*a*). If nitrogen is absent, add $AgNO_3$ solution. A white and curdy precipitate soluble in dilute ammonia confirms the presence of chlorine.

(*b*). If nitrogen *is present*, transfer part D into a dish, add to it about 1 c.c. of conc: HNO_3 and boil for a few minutes. Extract it with a little distilled water. Next add $AgNO_3$ solution to the extract. A white and curdy precipitate, soluble in dilute ammonia, confirms the presence of chlorine.

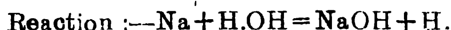
Chemistry of detection of these elements in an organic compound :—

Reactions of Sodium in the ignition tube.

The sodium, when heated carefully with the organic substance, combines with carbon and nitrogen of the substance to form sodium cyanide, and with sulphur and halogen, it forms sodium sulphide and halide respectively.

1. $Na + C + N = NaCN$.
2. $2Na + S = Na_2S$.
3. $Na + Cl = NaCl$.
4. $Na + Br = NaBr$.
5. $Na + I = NaI$.

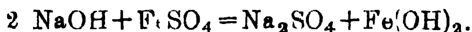
When the tube after ignition, is crushed in a dish containing a little water, the excess of sodium, if any, decomposes water liberating hydrogen, which may be inflamed, if tha tube is hot. Hence, the tube should be cooled before it is crushed.


Reaction :—$Na + H.OH = NaOH + H$.

On boiling, the sodium compounds which are formed during the ignition go in solution.

Reactions during the detection of Nitrogen in Part A.

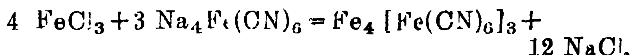
The sodium hydroxide acts on ferrous sulphate, forming sodium sulphate and a green precipitate of ferrous hydroxide :—


$2\ NaOH + FeSO_4 = Na_2SO_4 + Fe(OH)_2$.

On boiling, the ferrous hydroxide reacts with sodium cyanide, forming sodium ferrocyanide and sodium hydroxide :—


$Fe(OH)_2 + 6NaCN = Na_4\ Fe(CN)_6 + 2NaOH$.

On acidifying the solution in cold, the ferric chloride reacts with sodium ferrocyanide, precipitating a complex compound called *Prussian Blue*, which if present in traces dissolves, giving only a green solution :—


$4\ FeCl_3 + 3\ Na_4Fe(CN)_6 = Fe_4\ [Fe(CN)_6]_3 + 12\ NaCl$.

Reactions during the detection of Sulphur in Part B.

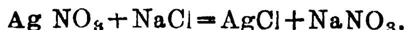
Sodium sulphide, if present, acts on sodium nitroprusside, forming a violet complex compound whose constitution is uncertain.

Reactions during the detection of Bromine and Iodine in Part C.

From all bromides or iodides, chlorine is able to replace respectively bromine or iodine, which dissolves in chloroform, imparting to it, brown or violet colour.

Reactions in the detection of chlorine in Part D.

In the absence of sodium cyanide, the $AgNO_3$ solution acts on NaCl giving a white and curdy precipitate of silver chloride which is soluble in dil ammonia :—



$$AgNO_3 + NaCl = AgCl + NaNO_3.$$

If sodium cyanide, *is present* it must be decomposed by strong nitric acid; and the hydrocyanic acid so formed should be removed by boiling, before adding $AgNO_3$. solution, otherwise, there will be a white precipitate of AgCN soluble in dil ammonia.

Quantitative Analysis.

Quantitative analysis usually follows the qualitative. It is necessary, therefore to consider the quantitative estimation of carbon, hydrogen. halogen, sulphur and nitrogen in an organic substance.

A. Estimation of Carbon and Hydrogen.



Liebig

Liebig's Method :—

This method is used for the estimation of carbon and hydrogen. The apparatus, in which these two

elements are quantitatively estimated, is a long hard glass tube known as a combustion tube, in which a weighed amount of the given substance taken in a boat (C) is strongly heated in a combustion furnace. A current of oxygen gas free from CO_2 and moisture. is passed through one end (a) of the tube. The products of combustion namely water vapour and carbon-dioxide are absorbed respectively in the U-tube containing fused $CaCl_2$ and the potash bulb, (both separately weighed) which are connected to the other end (b) of the tube.

The entire arrangement of the apparatus is shown in Fig. 10 continued with Fig. 11.

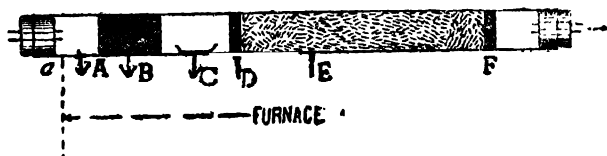


Fig. 10.

(1) From (a) to (A) is an air space.
(2) B is the oxidised copper roll.
(3) C is the boat containing X grams of the organic substance under examination.
(4) D is the oxidised copper roll.
(5) E is the cuppric oxide.
(6) F is the oxidised copper roll.
(7) From (F) to (b) is an air space.

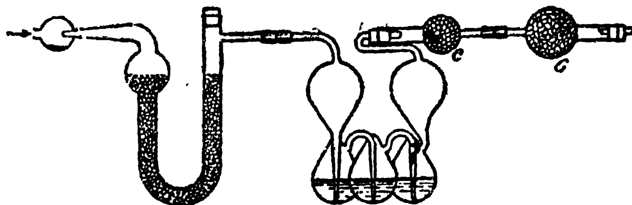


Fig. 11.

(8) The U-tube containing fused $CaCl_2$ absorbs moisture.

(9) The potash bulb absorbs CO_2.

After the complete combustion of the substance the supply of oxygen gas is cut off and air free from H_2O and CO_2 is passed through the apparatus for some time. Next, the U-tube and the potash bulb are detached and weighed again. The difference in the second and the first weighings of the U tube gives the weight of H_2O and that of the potash bulb the weight of CO_2 formed from the known weight of the substance under examination.

Calculation of the percentage of carbon and hydrogen in the substance.

Let X grams be the weight of the substance.
Y grams be the weight of H_2O formed,
Z grams be the weight of CO_2 formed.

For calculating the percentage of carbon, we know from the molecular formula of CO_2 that,

44 grams of CO_2 contain 12 grams of carbon.

$\therefore$ 1 gram of CO_2 contains $\frac{12}{44}$ gram of carbon.

$\therefore$ Z grams of CO_2 contain $\frac{12 \times Z}{44}$ grams of carbon.

Hence, X grams of the substance contain $\frac{12 \times Z}{44}$ grams of carbon.

$\therefore$ 1 gram of the substance contains $\frac{12 \times Z}{X \times 44}$ grams of carbon

$\therefore$ 100 grams of the substance contain $\frac{12 \times Z \times 100}{X \times 44}$ grams of carbon

Likewise.

For calculating the percentage of hydrogen, we know from the molecular formula of H_2O that,

18 grams of H_2O contain 2 grams of hydrogen.

∴ 1 gram of H_2O contains $\frac{2}{18}$ gram of hydrogen.

∴ Y grams of H_2O contain $\frac{2 \times Y}{18}$ grams of hydrogen.

Hence,

X grams of the substance contain $\frac{2 \times Y}{18}$ grams of hydrogen.

∴ 1 gram of the substance contains $\frac{2 \times Y}{18 \times X}$ grams of hydrogen.

∴ 100 grams of the substance contain $\frac{2 \times Y \times 100}{18 \times X}$ grams of hydrogen.

B. Estimation of Halogen.

Carius' Method :—

A thick-walled tube sealed at one end is selected A few c. c. of fuming nitric acid and a little of silver nitrate are introduced into it. Next a weighed amount of the substance taken in a small and narrow tube is gently and carefully slipped in. The free end of the thick-walled tube is drawn out to a jet and then sealed. This tube is next placed horizontally into a special hot-air furnace and heated at 200°C for 6 hours. The furnace is then cooled to room temperature. The tube is taken out of it and the jet end is carefully filled off. The contents are washed out into a breaker carrying all the precipitate of silver halide, which is separated by filtration, dried and weighed.

From the weight of the silver halide, the weight of halogen is calculated as usual.

C. Estimation of Sulphur.

Carius' Method :—

The procedure for the estimation of sulphur is the same as just described for the estimation o halogen with the difference, that in this case silver nitrate is not taken in the thick walle tube. After heating the tube in the hot-air furnace, its contents are washed out into a beaker. The solution in the beaker contains the entire amount of the sulphur present in the substance as H_2SO_4, which is precipitated as $BaSO_4$ by adding a solution of $BaCl_2$ to it. The precipitate is filtered, washed, dried and weighed. From the weight of $BaSO_4$, the weight of sulphur is calculated as usual.

D. Estimation of Nitrogen.

There are two methods in use for the estimation of this element.

1. Dumas' method,
2. Kjeldahl's method.



J. B. Dumas

1. *Dumas Method*

This method is described diagrametically as noted below :—

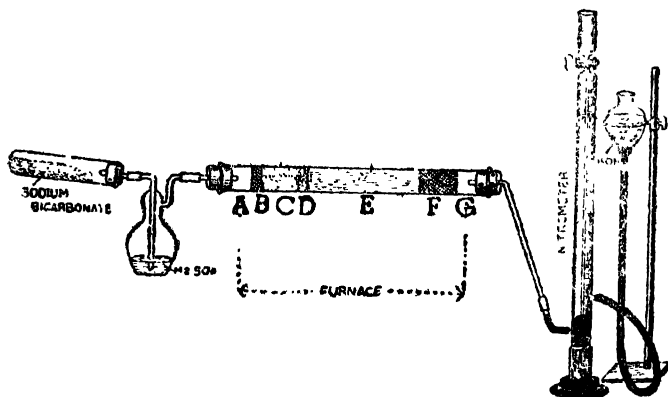


Fig. 12

(1). The tube containing sodium bicarbonate on being heated evolves CO_2.
(2). The wash bottle containing strong H_2SO_4 dehydrates CO_2.
(3). A to G is the combustion tube.
(4). B is the oxidised copper coil.
(5). C is a mixture of fine CuO and X grams of the substance under examination.
(6). D is ne fine CuO.
(7). E is CuO in the wire form.
(8). F is the reduced copper coil.

A known quantity of the substance, say *X* grams mixed with enough of CuO, is heated in a combustion tube AG over a furnace, and a current of dry CO_2 from the $NaHCO_3$ tube is swept through the combustion tube. As the substance is heated with cupric oxide (CuO), the entire amount of nitrogen present in it is oxidised to nitrogen oxide, which is next reduced by heated copper spiral to nitrogen. The

nitrogen gas so librated is collected over a strong solution of KOH into the graduated nitrometer (attached to the end G of the tube A G). The KOH solution absorbs CO_2. The nitrometer gives the volume of nitrogen evolved from X grams of the substance at certain temperature and pressure. This volume is reduced at N. T. P.

Suppose the volume of nitrogen collected in the nitrometer at t_1°C and P_1 m m pressure is V_1.

Now applying Boyle's and Charles' Law.

$$\frac{V_1 \times P_1}{T_1} = \frac{V_0 \times P_0}{T_0}$$

We have,

$$\frac{V_1 \times P_1}{273+t_1} = \frac{V_0 \times 760}{273}$$

$$\text{or} \quad V_0 = \frac{273 \times V_1 \times P_1}{760 \times (273+t_1)} \text{ c. c. at N. T. P.}$$

From Avagadro's hypothesis, we know that 22·4 litres of nitrogen at N. T. P. weigh 28 grams,

or 22400c.c. of nitrogen at N. T. P. weigh 28 grams.

or 1c.c. of nitrogen at N. T. P. weighs $\frac{28}{22400}$ gram.

$$\therefore \frac{273 \times V_1 \times P_1}{760 \times (273+t_1)} \text{ c c. at N. T. P. weigh}$$

$$\frac{28 \times 273 \times V_1 \times P_1}{22400 \times 760 \times (273+t_1)} \text{ grams.}$$

Hence,

X grams of the substance contains.

$$\frac{28 \times 273 \times V_1 \times P_1}{22406 \times 760 \times (273+t_1)} \text{ grams of nitrogen.}$$

$\therefore$ 1 gram of the substance contain.

$$\frac{28 \times 273 \times V_1 \times P_1}{22400 \times 760 \times (273+t_1) \times X} \text{ grams of nitrogen.}$$

∴ 100 grams of the substance contain.

$$\frac{28 \times 273 \times V_1 \times P_1 \times 100}{22400 \times 760 \times (273 + t_1) \times X} \text{ grams of nitrogen.}$$

(2) *Kjeldahl's method :—*

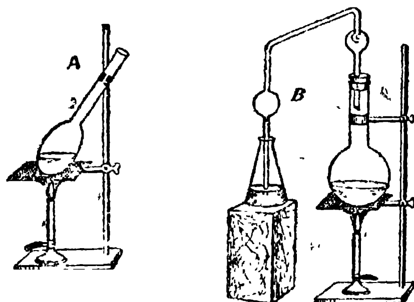


Fig. 13

X grams of the substance is heated strongly with K_2SO_4 and H_2SO_4 in excess in a round bottom flask having a long neck (Fig. 13 A.) The potassium sulphate helps the oxidation of C and H present in the substance to CO_2 and H_2O, while the entire amount of the nitrogen is converted into ammonia NH_3. The ammonia so evolved acts on the excess of H_2SO_4 in the flask A and is converted into ammonium sulphate.

After the completion of the reaction as indicated by the disappearance of the dark colour of the mixture, the colourless mixture of the flask A is transferred carefully into a distilling arrangement, (Fig. 13 B), and is distilled with an excess of caustic soda solution. The entire ammonia NH_3 so evolved is absorbed in a measured volume of a standard acid solution in excess in a conical flask (Fig 13). The excess of the acid in the conical flask is next neutralized by a standard solution of an alkali. Finally, the amount of nitrogen is calculated volumetrically in the usual way.

CHAPTER II.

Systematic study of Open chain compounds. (Saturated Series).

The open chain compounds are classified into the following families :—

(1). **Hydrocarbons** are the compounds of C and H elements only.

(2). **Halogen derivatives** of the hydrocarbons are the compounds of C, H and the halogen elements only.

(3). **Alcohols** are the compounds of C, H and O elements only.

(4). **Aldehydes and Ketones** are the compounds of C, H and O elements only.

(5). **Fatty Acids** are the compounds of C, H and O elements only.

(6). **Esters and Salts** are the compounds of C, H and O elements. The salts have in addition to these Na. K, Ca, Mg and N also.

(7). **Amides,** are the compounds of C. H, O and N elements only.

(8). **Cyanides,** are the compounds of C, H and N elements only.

(9). **Amines** are the compounds of C, H O and N elements only.

(10) **Acid Chlorides,** are the compounds of C, H, O and Cl elements only.

(11). **Acid Anhydrides,** are the compounds of C, H and O elements only.

(12). **Ethers** are the compounds of C, H and O elements only.

We shall consider these twelve **families** one after another in the subsequent chapters.

In making the study of these *families*, we have considered in this work, tho nomenclature, molecular and graphic formulæ of its various members: and discussed in detail their general methods of preparation as also their general properties followed by its application in the study of the first two *typical* members of each group. Towards the close of chapters devoted to the various families, the manufactur (only of the compounds prescribed) distinctive tests and uses of the typical members have also been dealt with.

CHAPTER III.

Hydrocarbons

We **have** already made ourselves familiar with the first five members of this family. These five members are (1) **Methane** (2) **Ethane** (3) **Propane** (4) **Butane** (5) **Pentane**. The molecular formulæ of these and other higher hydrocarbons can be derived from a general formula $C_n H_{2n+2}$, where the value of "n" may be 1, 2, 3, 4, 5 and so on. The molecular formulæ of the first five members of hydrocarbons are thus noted below :—


(1) Methane $= CH_4$


(2) Ethane $= C_2H_6$


(3) Propane $= C_3H_8$


(4) Butane $= C_4H_{10}$


(5) Pentane $= C_5H_{12}$

The next higher hydrocarbons are hexane, heptane, octane, nonane and decane, having 6, 7, 8, 9 and 10 carbon atoms respectively in their molecules. Theoretically, there may be any number of hydrocarbons; but we shall deal with only the first few of them in this book.

In the study of organic compounds their molecular formulæ alone do not suffice for our purposes. We need know the **Structural or Graphic Formulae** as well. The graphic formulæ of compounds lead to a clear understanding of the constitutional structures, not only of the parent substances but also of their derivatives.

Graphic formulae of the hydrocarbons

Alkyls :—By dropping out any atom of hydrogen from the molecular formula of a hydrocarbon, one gets to a monovalent radical called an *alkyl* of the corresponding hydrocarbon. These monovalent *alkyls* are only hypothetical groups of carbon and hydrogen atoms capable to enter into a chemical change. The name of such an alkyl is obtained by replacing the suffix "*ane*" of a hydrocarbon with the suffix "*yl*".

Table No: 1 shows the relation of the first five hydrocarbons to their monovalent alkyls.

Table No. 1

No.	Hydrocarbons.		Their monovalent alkyls	
	Names.	Molecular formulæ.	Names.	Formulæ
1.	Methane.	CH_4.	Methyl.	CH_3—
2.	Ethane.	C_2H_6.	Ethyl.	C_2H_5 -
3.	Propane.	C_3H_8.	Propyl.	C_3H_7 —
4.	Butane.	C_4H_{10}.	Butyl.	C_4H_9—
5.	Pentane.	C_5H_{12}.	Pentyl.	C_5H_{11}—

Methane, Ethane and their Alkyls compared graphically in table No. 2.

Table No. 2

Hydrocarbons	Graphic formulaæ	Name of the alkyls.	Graphic formulæ of the alkyls
1. Methane	H | H—C—H | H	1. Methyl	H | H—C— | H
2. Ethane	H H | | H—C—C—H | | H H	2. Ethyl	H H | | H—C—C— | | H H

Methane and *Ethane* give only one "alkyl" each ; because, in a molecule of methane, there is only one carbon atom; and in a molecule of ethane, there are two carbon atoms which are symmetrical. Hence, if we drop out any one out of the 4 atoms of hydrogen in methane, or any one out of the 6 atoms in ethane, in each case, we get identical alkyls. In the third hydrocarbon, *propane*, however, we shall get two different alkyls for the following reasons :—

Propane.



In *propane* the carbon atom in the middle is directly linked to two carbon atoms, Hence the "alkyl" of propane, known as "Normal Propyl" obtained by dropping out any one of the three hydrogen atoms from the extremeties is different from that, which is obtained by dropping out any one of the two hydrogen atoms from the middle carbon atom and this "alkyl" is hence known as "Iso-propyl".

Table No. 3.

The hydrocarbon	Graphic formulæ	Graphic formulæ of the two alkyls	Names of the alkyls.
Propane.	$\begin{array}{ccccccccc} & & H & & H & & H & & \\ & & \vert & & \vert & & \vert & & \\ H & - & C & - & C & - & C & - & H \\ & & \vert & & \vert & & \vert & & \\ & & H & & H & & H & & \end{array}$	(1) $\begin{array}{cccccccc} & & H & & H & & H & \\ & & \vert & & \vert & & \vert & \\ H & - & C & - & C & - & C & - \\ & & \vert & & \vert & & \vert & \\ & & H & & H & & H & \end{array}$	**"Normal Propyl"**
		(2) $\begin{array}{ccccccccc} & & H & & H & & H & & \\ & & \vert & & \vert & & \vert & & \\ H & - & C & - & C & - & C & - & H \\ & & \vert & & \vert & & \vert & & \\ & & H & & & & H & & \end{array}$	**"Iso Propyl"**

Note.—The alkyls of butane shall have to be considered at a later stage.

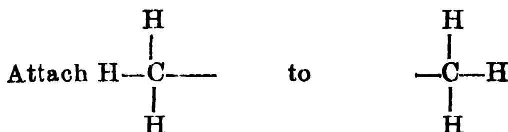
Having learnt about the "alkyls" of *Methane*, *Ethane* and *Propane*, we can write the graphic formulæ of (1) Ethane, (2) Propane and (3) Butane by adopting the following general principle :—

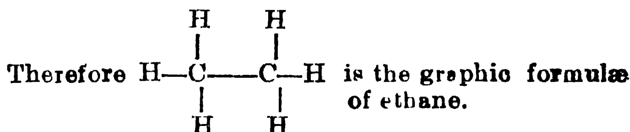
The graphic formulæ of any hydrocarbon is written by attaching methyl [CH_3—] to the "alkyl" or "alkyls" of the *preceeding* lower hydrocarbon.

Application of this principle in writing the Graphic formulae of (1) Ethane, (2) Propane and (3) Butane.

(1) Ethane.

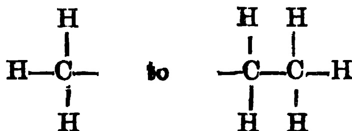
Attach methyl to the alkyl of methane

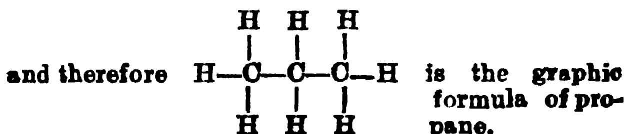




(2) Propane.

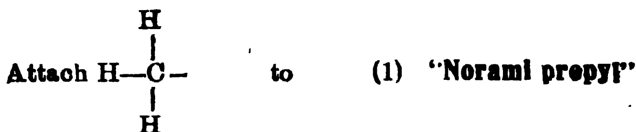
Attach methyl to the alkyl of ethane

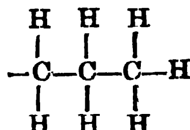




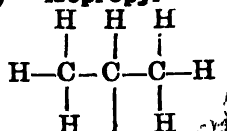
(3) Butane.

Attach methyl to the two alkyls of propane



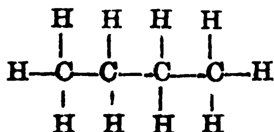


(2) "Isopropyl"

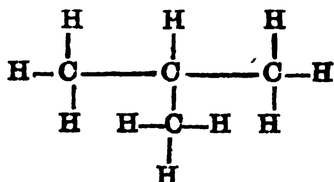


and therefore the two isomeric forms of butane are :—

(1) **Normal butane** from **"Normal Propyl"**



(2) **Isobutane** from **"Isopropyl"**

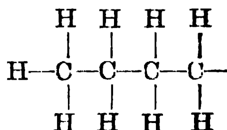


Alkyls of Butane.

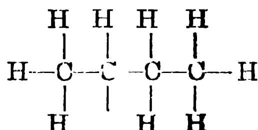
The two isomers of butane give four alkyls namely (1) Normal butyl (2) Isobutyl and (3) Primary isobutyl (4) Neobutyl.

The normal butane for reasons explained in propane gives two alkyls, namely :—

(1) **"Normal Butyl"**

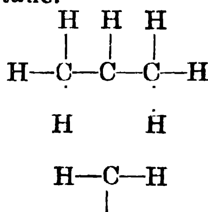


(2) **"Isobutyl"**



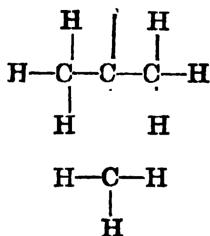
The alkyls derived from isobutane.

(3) **"Primary isobutyl"**



Since **Isobutane** has one carbon atom directly attached to three carbon atoms, there is a single hydrogen atom attached to this particular carbon atom. When this hydrogen atom is dropped out we get the fourth alkyl, namely."

(4) **"Neobutyl"**



:ane ur kyls compare phically in the No

Tab' No

The hydrocarbon.	Graphic formulæ	Graphic formulæ of the alkyls.	Names of their alkyls.
Normal butane	H H H H | | | | H—C—C—C—C—H | | | | H H H H	H H H H | | | | (1) H—C—C—C—C— | | | | H H H H	Normal butyl.
		H H H H | | | | (2) H—C—C—C—C—H | | | | H H H	Isobutyl.

The hydrocarbon	Graphic formulæ.	Graphic formulæ of the alkyls.	Names of their alkyls.
Isobutane ...	H H	H H—C—C—C—H H	H H—C—H H	H H	H (3) H—C—C—C—H H	H H—C—H |	Primary isobutyl.
			 H	H (4) H—C—C—C—H H	H H—C—H H	Neobutyl.

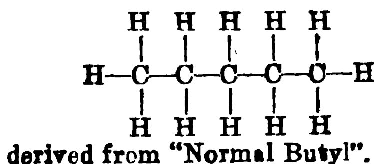
Although butane gives four alkyls, we shall consider here only *three isomers* of the next higher member **Pentane**, namely

(1) **Normal pentane,**
(2) **Isopentane,**
(3) **Neopentane.**

The graphic formulæ of the three pentanes can readily be written by attaching methyl to the **three alkyls of the butane.**

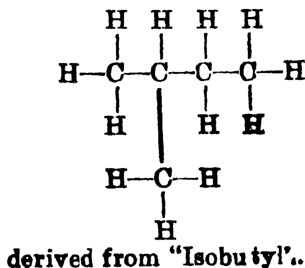
Isomers of Pentane.

(1) **Normal pentane**



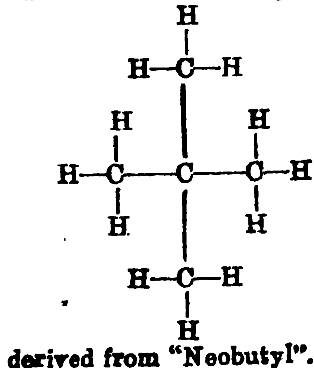
derived from "Normal Butyl".

(2) **Isopentane**



derived from "Isobutyl".

(3) **Neopentane**



derived from "Neobutyl".

From the study of the constitution of the two isomers of butane and the above three of pentane, we are in a position to define Normal, Iso and Neocompounds in general :—

Definition :—

Normal compounds are those which have *no carbon atom* in their molecules directly attached to more than two carbon atoms.

Isocompounds are those which have at least *one carbon atom* in their molecules directly attached to three carbon atoms.

Neocompounds are those which have at least *one carbon atom* in their molecules directly attached to four carbon atoms.

Summ y o e firs dro mers along with stru mu abl

b!e

No. I.	No. II.	No. III.	No. IV.
Hydrocarbons	Structural formulæ in abbreviate form.	Structural formulæ of their alkyls in abbreviate.	Name of the alkyls.
(1) **Methane**	$CH_3—H$	$CH_3—$	"Methyl".
(2) **Ethane**	$CH_3—CH_3$	$CH_3—CH_2—$	"Ethyl".
(3) **Propane**	$CH_3—CH_2—CH_3$.	(1) $CH_3—CH_2—CH_2—$	"Normal propyl".
(4) **Butane**		(2) $\begin{matrix} CH_3 \\ CH_3 \end{matrix} > \overset{H}{\overset{\mid}{C}}—$	"Isopropyl".

No. I.	No. II.	No. III	No. IV.
Hydrocarbons	Structural formulæ in abbreviate form.	Structural formulæ of their alkyls in abbreviate.	Name of the alkyls.
(1) **Normal butane**	$CH_3—CH_2-CH_2—CH_3$	(1) $CH_3—CH_2—CH_2—CH_2—$	"Primary normal butyl".
		(2) $CH_3—CH_2—CH_2—CH_3$ (with a bond from the second carbon)	"Isobutyl".
(2) **Isobutane**	H $CH_3—C—CH_3$ CH_3	H $CH_3—C—CH_2—$ CH_3	"Primary isobutyl"
		$CH_3—C—CH_3$ (with an open bond above) CH_3	"Neobutyl".

Note :—Taking into consideration of columns No: III and IV in table No. 5 pages 43 and 44 we can easily get to the general formulæ of the chlorine derivatives of the hydrocarbons, namely alkyl chlorides by attaching one atom of chlorine to the corresponding "alkyls", such as :—

(1) CH_3—Cl Methyl chloride.

(2) C_2H_5—Cl Ethyl chloride.

(3) CH_3 CH_2—Cl Normal propyl chloride and

$$\begin{matrix} CH_3 \\ CH_3 \end{matrix} > \underset{\underset{H}{|}}{C} — Cl$$ Isopropyl chloride and so on.

Hence, the general formula of an alkyl halide is R—X, where,

R="alkyl",

X=Cl, Br or I.

General methods for the preparation of hydrocarbons.

Note :—The first general method for the preparation considered in the book for the members of the various families, will invariably be the laboratory method for their preparation.

The first general method.

It consists in heating a mixture of fused sodium salt of the corresponding fatty acid and caustic soda (sodium hydroxide).

To follow this general method, let us first of all derive the general formulæ for the sodium salt of fatty acids.

Fatty Acids.

Name and molecular formulae of some of the common fatty acids.

(1) Formic acid = $H. COOH$.

(2) Acetic acid = $CH_3. COOH$.

(3) Propionic acid = $C_2H_5. COOH$.

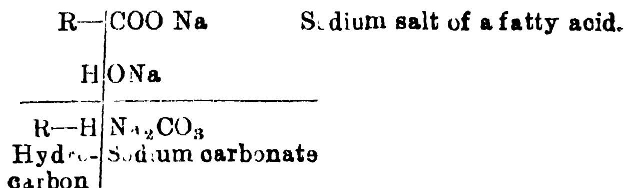
....

....

(4) Palmitic acid = $C_{15}H_{31}.COOH$. } Higher
(5) Stearic acid = $C_{17}H_{35}$ $COOH$. } fatty acids.

[We find here that the monovalent **carboxylic group** (—COOH) is a common factor in all the fatty acids. Therefore, R COOH may be taken as a general formula for fatty acids; where R stands mostly for an alkyl group. Since the sodium salt of a fatty acid is obtained by the replacement of the hydrogen atom in the carboxylic group by one atom of sodium the general formula of the sodium salt of a fatty acid is R.COO Na.]

Thus, when the sodium salt of a fatty acid is heated with NaOH, we shall have the following general reaction :—

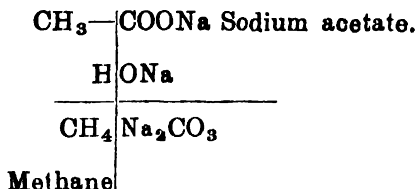


Note :—The letter R stands for an "alkyl" like "Methyl" or "Ethyl" etc. throughout this book.

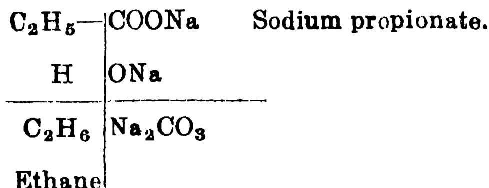
Preparation of methane and ethane by the above method.

(a) By heating a mixture of sodium acetate and sodium hydroxide, we prepare methane.

Raaction.



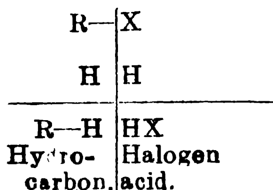
(b) By heating a mixture of sodium propionate and sodium hydroxide, we can prepare ethane.



The second general method.

It consists in treating an alkyl halide with nascent hydrogen.

General Reaction.

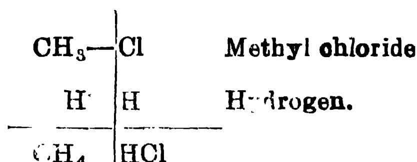


Note :—The letter "X" stands for the halogen (Cl, Br or I) through out this book.

Preparation of methane and ethane by the above method.

(a) By reducing methyl chloride with the nascent hydrogen, we can prepare methane.

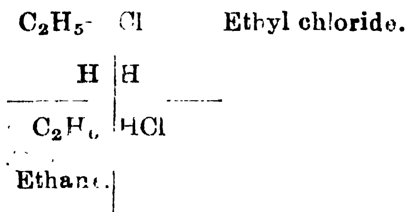
Reaction.



Methane

(b) By reducing ethyl chloride with the nascent hydrogen, we can prepare ethane.

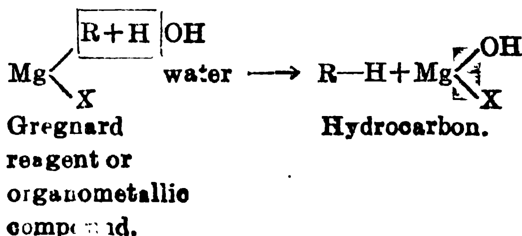
Reaction.



The third general method.

It consists in hydrolysing the Gregnard reagent (organometallic compound).

General Reaction.



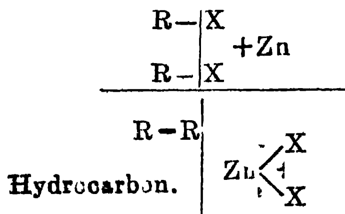
Preparation of Methane and Ethane by the above method.

By the hydrolysis of the "methyl" and "ethyl" derivatives of the Gregnard reagent, we can prepare methane and ethane respectively. By substituting the alkyl CH_3—or C_2H_5—for R in the above general reaction, we can easily get the reactions for the preparations of methane and ethane.

The fourth general method.

It consists in distilling zinc or sodium with an alkyl halide (*Wurtz Reaction*).

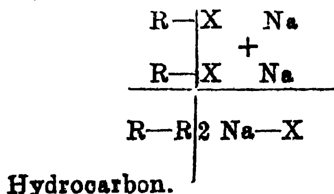
General Reaction.



$$\begin{array}{l} R-X \\ R-X \end{array} + Zn = R-R + ZnX_2$$

Hydrocarbon.

or,



$$\begin{array}{l} R-X \\ R-X \end{array} + \begin{array}{l} Na \\ Na \end{array} = R-R + 2\,Na-X$$

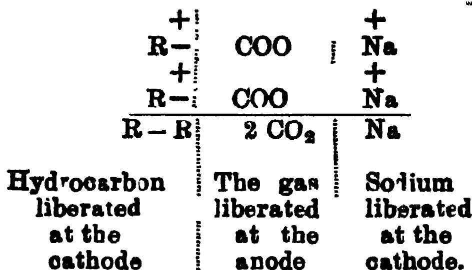
Hydrocarbon.

Note :—This reaction is a great help in synthesising the next higher homologue from a lower hydrocarbon.

The fifth general method :—

It consists in the electorlysis of sodium salts of fatty acids. [*Kolbes Reaction.*]

General Reaction.



Notes :—On the fourth and fifth general method :—

(1). Two molecules of an alkyl halide or the sodium salt of a fatty acid, shall have to be considered in these reactions.

(2) In expressing the reactions, the letter R in the formulæ of the two molecules of the alkyl halides or of the sodium salts of the fatty acids, may stand for the alkyl of the same or of the two different hydrocarbons. For example, in the reactions for the preparation of ethane by the last two methods, the letter "R" will stand for methyl in both the molecules; but in the preparation of propane, the letter "R" will stand in one molecule for methyl and in the other molecule for ethyl.

(3) Methane, the parent hydrocarbon, cannot be prepared by the last two methods.

General Properties of the Hydrocarbons.

Physical.

(1). The hydrocarbons—methane to pentane are all odourless and colourless gases. The next eleven

higher hydrocarbons are liquid, having no colour and no odour. The rest of them are solid.

(2). All the hydrocarbons are insoluble in water; but they are soluble in organic solvents like alcohols or ether. The solubility of the hydrocarbons in these solvents decreases as the molecular weight of the former increases.

(3). They are lighter than water.

Chemical.

1. They are comparatively inactive compounds, and do not act even on conc: H_2SO_4 and HNO_3. Caustic soda or potash and even strong oxidising agents have ordinarily no effect on them. Hence, they are known as *paraffins*, [From Latin Parum = very little and affins = activity.]

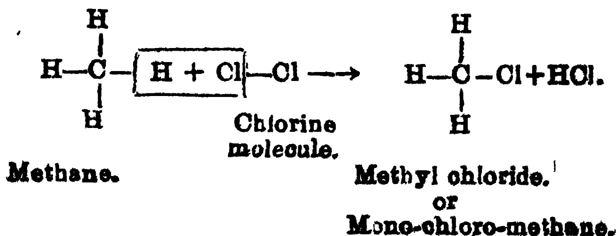
2. They, however, burn in air forming CO_2 and H_2O.

3. They only give substitution products with halogen *except iodine.*

Chlorine are bromine may replace one, two or more hydrogen atoms of the hydrocarbons, yielding mono di, tri and poly derivatives as examplefiled in the following reactions of chlorine with methane or marsh gas which is the parent hydrocarbon :—

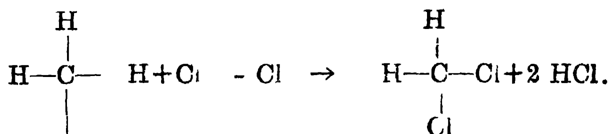
(1). The Mono-Chloro-derivatives of Methane.

(One molecule of chlorine acting on a molecule of Methane.)



(2). The Di-chloro-derivative of Methane.

(Two molecules of chlorine acting on a single molecule of Methane)

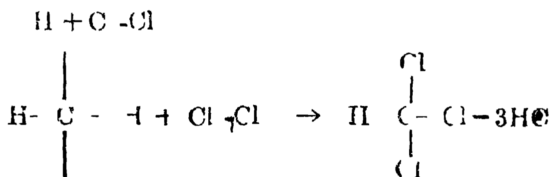


$$\mathrm{CH_4 + 2\,Cl{-}Cl \rightarrow CH_2Cl_2 + 2\,HCl}$$

Methane. → Methylene chloride or Di chloro-methane

(3). Tri-chloro-derivative of Methane.

(Three molecules of chlorine acting on a single molecule of Methane.)

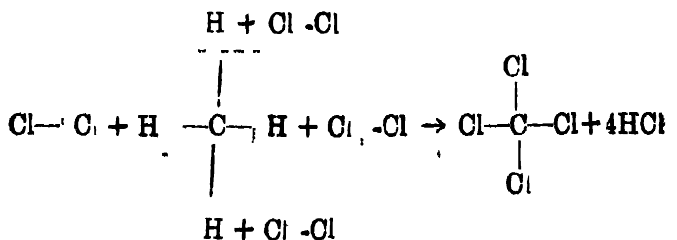


$$\mathrm{CH_4 + 3\,Cl{-}Cl \rightarrow CHCl_3 + 3HCl}$$

Methane. → Tri-chloro methane or Chloroform

4. The Tetra chloro derivative of Methane.

(Four molecules of chlorine acting on a single molecule of Methane]



Methane. Tetra-chloro-methane or Carbon-tetra-chloride.

Bromine will give similar four corresponding products Chlorine or bromine will react with other hydrocarbons also, giving substitutive products. *Iodine does not act on hydrocarbons.*

Methane

1 Laboratory Method for the Preparation of Methane

It consists in heating a mixture of fused (anhydrous) sodium acetate and soda lime, (a mixture of NaOH and CaO) in a flask, fitted with a delivery tube as shown in the figure No. 14.

The gas, being insoluble in water, is collected over water.

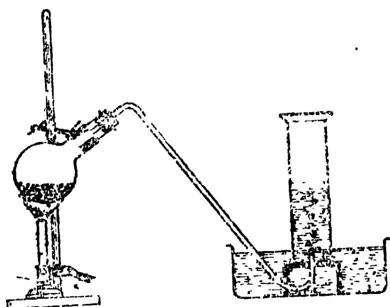
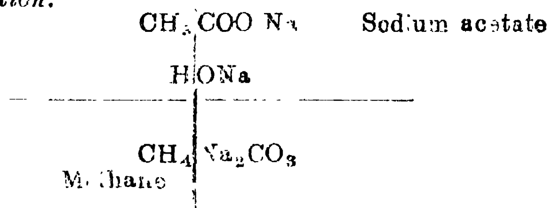


Fig. No. 14

Reaction.



Note : —The object of using CaO along with NaOH, is to prevent caking of the mass.

This method is also applicable for the preparation of ethane, with the modification, that in that case we have to heat a mixture of sodium propionate and soda lime.

2. *Method.*

It consists in decomposing aluminium carbide (Al_4C_3) with dilute hydrochloric acid. Take a little of aluminium carbide in a conical flask fitted up, with a dropping funnel and a delivery tube. The hydrochloric acid is allowed to drop from the funnel D on the carbide. The gas is collected over water as usual [Fig. No. 15]

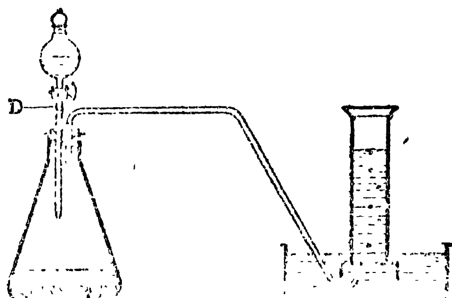


Fig. No. 15

Reation.



$Al_4C_3 + 12HCl \rightarrow 4\ AlCl_3 + 3CH_4$ (Methane.)

Some Special Chemical Properties of Methane.

1. Methane mixed with phosphorus tetrahydride (P_2H_4) is spontaneously inflammable. Occasional fitful flames on the surface of marshy lands, are due to the fact, that, during the decomposition of vegetable matter in marshy places, the marsh gas is evolved mixed with traces of phosphorus tetrahydride (P_2H_4) which is formed by the action of water on carbides present in a marshy land. The phosphorus tetrahydride being spontaneously inflammable we abserve fitful flames.

(2). Methane mixed with air, oxygen or chlorine explodes on ignition.

The chapter on hydrocarbons will remain incomplete without the study *of Petroleum*, which is the only natural source for the various hydrocarbons used as fuels, lubricants illuminants and for other purposes.

Petroleum

Occurrence :—

Petroleum occurs in its crude form as a drak brown viscous liquid mixture, generally associated with natural gas, consisting mostly of the lower hydrocarbons, like methane, deep in the interior of the earth, over widely distributed areas of the world, chiefly in America, Russia, Dutch East Indies and Burma, which have a rich oil fields. In India also small quantity of petroleum is found near Attock in the Punjab.

Origin ot the Petroleum in the interior of the Earth.

There are two theories :—

1. Mendeleeff's theory :—

The action of steam on various carbides in the interior of earth resulted ultimately in the formation of petroleum.

Reaction :—$CaC_2 + H_2O \rightarrow CaO + C_2H_2$ (acetylene)

The acetylene subsequently polymerised into more complex hydrocarbons (petroleum).

2. Engler's theory :—

The remains of sea animals of prehistoric ages, under the pressure of thick layers of mud and rocks, were decomposed and ultimately converted into petroleum oil.

As the result of great geological changes in the strata of the upper earth crust, the petroleum bearing rocks were carried deep into the interior of the earth. The petroleum parcolated through rocks, and collected in the subterranean reservoirs, mostly on the surface

of salt water. The petroleum deposits are generally found to be capped with natural gas (lower hydro-carbons), under great pressure as shown in Fig. 16

Engler was led to put forward his hypothesis of the organic origin of petroleum from his experiment in 1900, when he discovered that the destructive distillation of the fish bladder gave a liquid like petroleum.

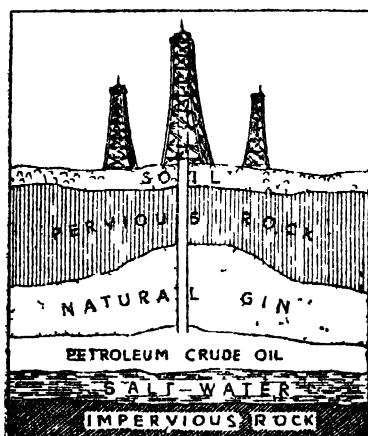


Fig No. 16

The Petroleum Industry :—

Petroleum oil in crude form is brought to the surface by boring down to the subterranean reservoirs. Since the oil deposits are generally capped with natural gases under great pressure, the gases rush out with great violence, carrying thick columns of the oil to great heights, when the bore is first drilled for obtaining the crude oil; but, later or, when the internal pressure, is greatly reduced, the crude petroleum oil has got to be pumped out and carried to the refineries.

Refining of crude Petroleum.

The crude petroleum is fractionally distilled in an iron retort connected with condensers A and B as shown in Fig. 17. The distillates are collected in different reservoirs at different ranges of temperature.

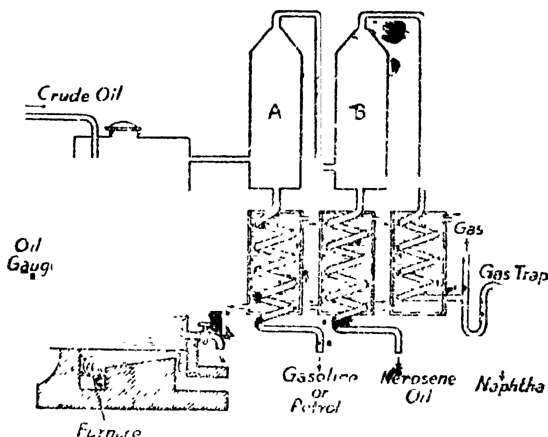


Fig. 17.

The following are the distillates collected :—

1. Gasoline or petrol collected from the condenser A between 30°C to 200°C. It is a liquid mixture of pentane, hexane, heptane and benzene etc. and is used as a fuel for internal combustion engines.

2. Kerosine oil collected from the condenser B between 200°C to 360°C. It is a mixture of liquid hydrocarbons between $C_{10}H_{22}$ and $C_{15}H_{32}$, used as an illuminating mineral oil.

3 The gases from the condenser B are further cooled and condensed as a heavy oil, the gases which, however, do not condense are the hydrocarbons—methane to butane which are collected in gas holders and used as gas fuel.

4. Crude oil is the commercial name of the residue left in the distilling retort.

Treatment of the Crude Oil.

It is subjected to two processes.

(1) Distillation under reduced pressure.

(2) Cracking.

(1). Distillation under Reduced pressure.

When this crude oil is distilled under reduced pressure, the distillate is a lubricating oil containing paraffin wax, which is separated by freezing and pressing.

(2). Cracking.

The crude oil is distilled at a high pressure (800 lbs per square inch) and temperature between 800°C to 1240°C). This process is known as *Cracking*, during which, the higher hydrocarbons in the crude oil are decomposed into lower and more volatile hydrocarbons more suitable for use as petrol. As for example :—

The hexadecane ($C_{16}H_{34}$) which is a higher hydrocarbon can not be used as a motor fuel, being less volatile. On being cracked, the molecule of hexadecane is ruptured in the middle of the carbon chain, yielding decane, which is a lower hydrocarbon, and is quite suitable for motor fuel being more volatile.

Note :—Petroleum Benzine (not to be confused with benzene which is an aromatic hydrocarbon) is also obtained from the fractional distillation of the crude petroleum between 120°C and 150°C. Benzine is largely used in dry cleaning.

Synthetic Petroleum :—In Germany and Great Britain, large quantities of petroleum is being synthesised from powdered coal. The coal taken in a fine state of sub-division is made into a slurry with a heavy oil. Next, it is heated to 500°C in hydrogen at 200 atmospheric pressure in the presence of catalysts like molybdenum sulphide and tungstan oxide. The reaction is strongly exothermic.

CHAPTER IV.

Halogen derivatives of the Hydrocarbons or Alkyl Halides.

1. Monohalogen derivatives.

The hydrocarbons—methane and ethane give only one monohalogen-derivative, namely methyl halide (CH_3-X) and ethyl halide (C_2H_5-X).

But since propane has two and butane four alkyls, their monohalogen-derivatives exist in two and four different forms respectively.

The two Isomeric Halogen derivative of Propane.

1. The normal propyl halide.

$CH_3-CH_2-CH_2-X$, corresponding to the normal propyl.

2. The isopropyl halide.

$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!>\!\underset{\displaystyle H}{\underset{|}{C}}-X$$ corresponding to the isopropyl

The four Isomeric Halogen derivatives of Butane.

(1). The primary normal butyl halide.

$CH_3-CH_2.CH_2.CH_2-X$ corresponding to the primary normal butyl.

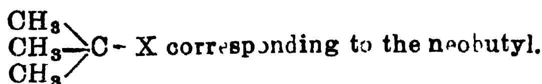
(2). The isobutyl halide.

$$\begin{matrix} CH_3 \\ C_2H_5 \end{matrix}\!>\!CH-X$$ corresponding to the isobutyl.

(3). The primary isobutyl halide.

$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!>\!\underset{\displaystyle H}{\underset{|}{C}}-CH_2-X$$ corresponding to the primary isobutyl.

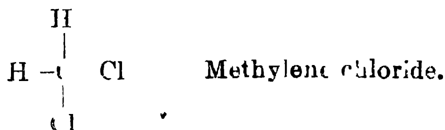
(4). The neobutyl halide.



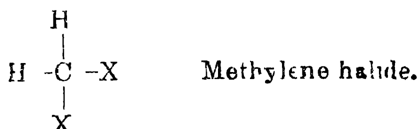
Note :—The monoh logen derivatives of the hydrocarbons are parent substances for preparing mono-hydroxy alcohols. (Read chapter V).

II. Dihalogen-derivatives.

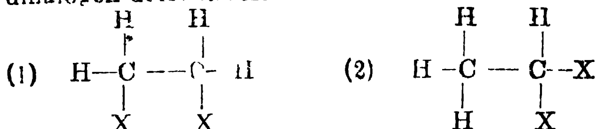
We have alre dy made ourselves familiar with methylene chloride as one of the di-halogen-derivative of methane.



Hence, the gen r l formula of the di-halogen derivative of methane will be.



Ethane shall however have two isomeric forms of its dihalogen derivatives.



Ethylene di-halide. The two X atoms attached to two different carbon atoms.

Ethylidene di-halide. The two X atoms attached to one and the same carbon atoms.

Note :—The di-halogen-derivatives of the hydrocarbons are the parent substances for obtaining dihydroxy alcohols. (Read chapter XV).

General method for the preparation of Alkyl Halides or Halogen derivatives.

(1). With the exception of alkyl iodides, other alkyl halides are prepared by the action of the halogen on the hydrocarbons. (Read page 53).

(2) By the action of halogen acids, HCl, HBr and HI on alcohols. [Read esterification chapter VIII].

General reactions of alkyl halides or the halogen derivatives

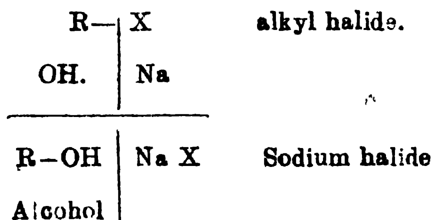
1. The reaction with nascent Hydrogen

Alkyl halides are reduced by nascent hydrogen; giving the corresponding hydrocarbons. [Read the second general method for the preparation of hydrocarbons page 47]

2. The reaction with aqueous caustic Soda (NaOH) or caustic Potash (KOH).

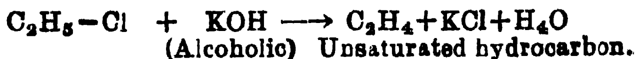
When caustic soda or potash dissolved in water acts on an alkyl halide, the **Hydroxyl group** (—OH) of the alkali replaces the halogen of the alkyl halide giving alcohols Read general method of the preparation of alcohols chapter V].

Reaction :—



3 The reaction of Alcoholic caustic soda or Potash.

When caustic soda or potash dissolved in the alcohol acts on an alkyl halide, we get an unsaturated hydrocarbon corresponding to the alkyl halide. [Read chapter on unsaturated hydrocarbons].



$C_2H_5-Cl + KOH \longrightarrow C_2H_4+KCl+H_4O$
(Alcoholic) Unsaturated hydrocarbon.

(4) The reaction of Ammonia.

When ammonia $(H-N_2)$ acts on an alkyl halide. the halogen attached to the alky is replaced by amino group $(-NH_2)$ forming amines. [Read charter XI on amines].

Reaction.



R— Alkyl halide.

NH_2— H Ammonia.



$R-NH_2$ HX Halogen acid.

Amine

(5) The reaction of Potassium cyanide (KCN).

When potassium cyanide acts on an alkyl halide, the halogen attached to the alkyl is replaced by cyanogen group. (—CN) forming cyanides. [Read chapter X on cyanides]

Reaction :-



R— Alkyl halide.

CN— Potassium cyanide.



R—CN K X Potassium halide.

Alkyl cyanide.

(6) The reaction with Silver Nitrite ($AgNo_2$).

When silver nitrite acts on an alkyl halide, the halogen of the alkyl halide is replaced by nitro group (NO_2) forming nitro-paraffin.

Reaction :—

R—	X	Alkyl halide.
NO_2—	Ag	Silver nitrite.
R—NO_2 Nitro-paraffin	AgX	Silver halide.

(7). The reactions with Sodium or Zinc.

[Read the fourth general method of preparation for hydrocarbons page 49].

Note :—(1) The di-halogen-derivatives likewise give the di-substitutive products with (*a*) nascent hydrogen (*b*) aqueous and alcoholic caustic soda or potash (*c*) ammonia (*d*) potassium cyanide and (*e*) silver nitrite forming (1) hydrocarbons, (2) *di hydroxy-alcohols.* [Read Chapter XV]. (3) diamines (4) dicyanides and (5) di-nitro-paraffins respectively.

Note :—(2) The typical halogen derivatives, as for example ethyl chloride and ethyl bromide prescribed in the syllabus will be considered in the chapter on esters.

CHAPTER V.

ALCOHOLS

Alcohols are compounds in which the alkyl group is attached to one or more hydroxyl groups (—OH). We get thus monohydroxy, dihydroxy, trihydroxy and polyhydroxy alcohols, according to the number of hydroxy groups attached to the alkyl group. We shall restrict ourselves at present to the study of monohydroxy alcohols.

Monohydroxy Alcohols.

General Formulae of the Various members of the Monohydroxy Alcohols.

The table on page 66 shows the relation of the alkyls of the hydrocarbons to the constitution of the corresponding alcohols to be studied:—

Table No. 6.

Serial No	No. I	No. II.	No. III.	No. IV.
	Alkyls.	Constitution of the alkyls.	Constitution of the alcohols along with their isomers.	Names of the alcohols.
1.	Methyl	$H-CH_2-$	$H-CH_2-OH$	1. Methyl Alcohol.
2.	Ethyl.	CH_3-CH_2-	CH_3-CH_2-OH	2. Ethyl Alcohol.
3.	Normal propyl	$C_2H_5-CH_2-$	Isomers. $C_2H_5-CH_2-OH$	3. Isomers. Primary propyl alcohol.
	Isopropyl	$\frac{CH_3}{CH_3}>C(H)-$	$\frac{CH_3}{CH_3}>C(H)-$	Secondary propyl alcohol.

4.	Normal butyl	$C_3H_7-CH_2-$	Isomers.	$C_3H_7-CH_2-OH$	4.	Primary butyl alcohol.	Isomers.
	Isobutyl	$\begin{matrix}CH_3\\C_2H_5\end{matrix}>\begin{matrix}C-\\\mid\\H\end{matrix}$		$\begin{matrix}CH_3\\C_2H_5\end{matrix}>\begin{matrix}C-OH\\\mid\\H\end{matrix}$		Secondary butyl alcohol.	
	Primary isobutyl	$\begin{matrix} & H & \\ & \mid & \\ CH_3- & C & -CH_3 \\ & \mid & \\ H- & C & -H \\ & \mid & \end{matrix}$		$\begin{matrix} & H & \\ & \mid & \\ CH_3- & C & -CH_3 \\ & \mid & \\ H- & C & -H \\ & \mid & \\ & OH & \end{matrix}$		Primary isobutyl alcohol.	
	Neobutyl	$\begin{matrix} & CH_3 & \\ & \mid & \\ CH_3- & C & - \\ & \mid & \\ & CH_3 & \end{matrix}$		$\begin{matrix} & CH_3 & \\ & \mid & \\ CH_3- & C & -OH \\ & \mid & \\ & CH_3 & \end{matrix}$		Tertiary butyl alcohol.	

Note :—From the study of the column III Table 6, we find that methy alcohol and ethyl alcohol, have the monovalent primary alcoholic group, Hence, they always behave as primary alcohols.

General Methods for the preparation of Alcohols.

1. The first General Method.

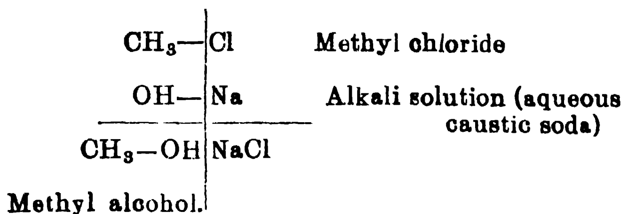
It consists in treating an aqueous caustic soda with the corresponding alkyl halide. [For the general reaction of this method refer to the second general property of alkyl halides page 62].

For example :—

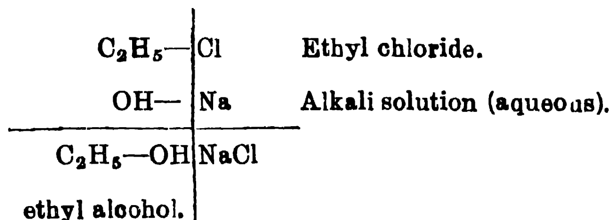
Preparation of Methyl and Ethyl Alcohols by the above method.

These alcohols are prepared by the action of aqueous solution of *caustic soda or potash on* methyl chloride and ethyl chloride.

(a) *Reaction.*



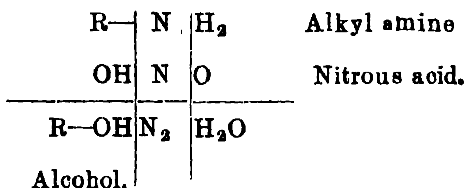
(b) *Reaction.*



2. The second General Method.

It consists in the treatment of an alkyl amine with nitrous acid (OH. NO).

General Reaction.



R—	N	H_2	Alkyl amine
OH	N	O	Nitrous acid.
R—OH	N_2	H_2O	
Alcohol.			

Note :—(1) In actual practice a mixture of $NaNO_2$ and H_2SO_4 is used for nitrous acid.

(2) It is an important reaction. It is used in converting an amine into an alcohol, or replacing amino group (—NH_2) in any organic compound by the hydroxyl group (—OH).

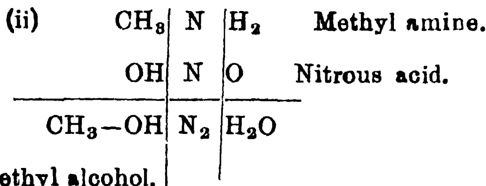
Preparation of Methyl and Ethyl Alcohols by the above method.

It consists in the treatment of a mixture of sodium nitrite and sulphuric acid with methyl and ethyl amines.

(a) *Reactions*



(i) $H_2SO_4+2\ NaNO_2=Na_2SO_4+2\ (OH.\ NO)$.



(ii)

CH_3	N	H_2	Methyl amine.
OH	N	O	Nitrous acid.
CH_3-OH	N_2	H_2O	
Methyl alcohol.			

(b) *Reactions.*



(i) $H_2SO_4+2NaNO_2=Na_2SO_4+2\ OH.\ NO)$.

(ii) C_2H_5 | N | H_2 Ethyl amine.

OH- N O Nitrous acid.

C_2H_5OH | N_2 | H_2O

Ethyl alcohol.

General properties of Alcohols.

Physical.

(1) The first four members of alcohols are colourless thin liquids possessing characteristic alcoholic smell and burning taste. They are all volatile. Higher alcohols are either oily liqu ds or waxy solids.

(2) They are soluble in water and in organic solvents, like ether, ch'oroform and acetone.

Chemical.

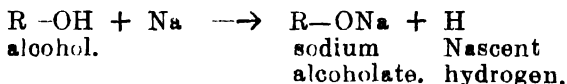
The General chemical Reactions.

[*Every general reaction will be illustrated by methyl and ethyl alcohols*).

1. The general reaction of alcohols on sodium or potassium.

When sodim or potassium acts on alcohols, the hydrogen atom of its hydroxyl (—OH) group is replaced by one atom of sodium or potassium forming sodium or potassium alcoholate.

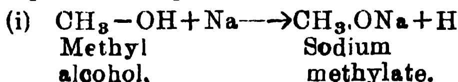
General reaction.



R –OH + Na ⟶ R—ONa + H

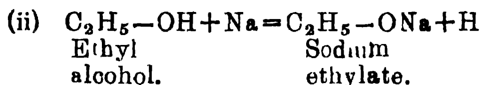
alcohol. sodium alcoholate. Nascent hydrogen.

The above general reaction illustrated in the case of Methyl and Ethyl Alcohols.



(i) $CH_3-OH+Na \longrightarrow CH_3.ONa+H$

Methyl alcohol. Sodium methylate.

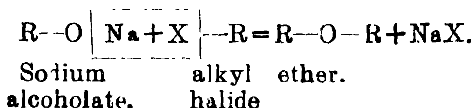


(ii) $C_2H_5-OH+Na=C_2H_5-ONa+H$

Ethyl alcohol. Sodium ethylate.

Note :—Sodium or potassium alcoholate acting on an alkyl halide forms ether, whose general formula is R—O—R.

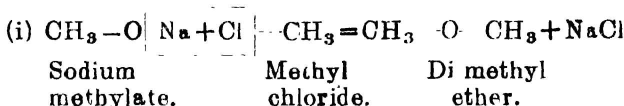
General Reaction.



$R-O\,|\,Na+X\,|\,-R=R-O-R+NaX.$

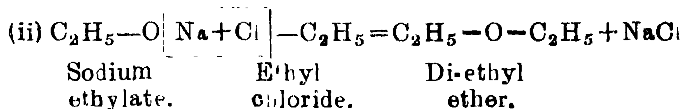
Sodium alcoholate. alkyl halide ether.

The above reactions are illustrated in the case of Sodium Methylate and Ethylate.



(i) $CH_3-O\,|\,Na+Cl\,|\,-CH_3=CH_3-O-CH_3+NaCl$

Sodium methylate. Methyl chloride. Di methyl ether.



(ii) $C_2H_5-O\,|\,Na+Cl\,|\,-C_2H_5=C_2H_5-O-C_2H_5+NaCl$

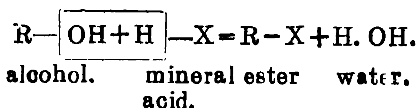
Sodium ethylate. Ethyl chloride. Di-ethyl ether.

2. *The general reaction of alcohols on a mineral or a fatty acid.* [*The mineral acid*=**HX** ; *the fatty acid*=**R. COOH**]

When a mineral or a fatty acid acts on an alcohol, the replaceable hydrogen atom of the former combines with the hydroxyl (–OH) group of the latter forming water. The alkyl group of the alcohol gets attached to the remaining group [–X or R.COO–] of the acids forming a compound called **Ester.**

Note.—This reaction is known as *Esterification*, which is an example of a reversible reaction, because the water formed here, is capable of hydrolysing the ester into the corresponding acid and the alcohol.

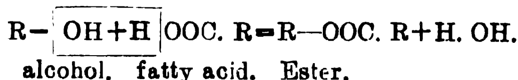
General Reaction.



$$R-\boxed{OH+H}-X = R-X + H.OH.$$

alcohol. mineral acid. ester water.

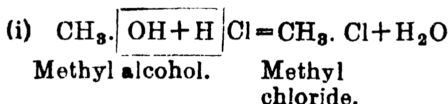
Or,



$$R-\boxed{OH+H}OOC.R = R-OOC.R + H.OH.$$

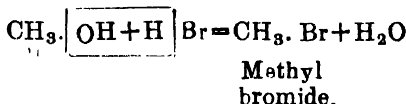
alcohol. fatty acid. Ester.

The above reactions are illustrated in the case of Methyl and Ethyl Alcohols acting on HCl, HBr and $CH_3.COOH$.



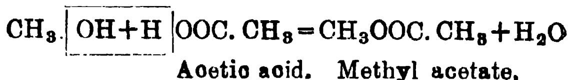
(i) $CH_3.\boxed{OH+H}Cl = CH_3.Cl + H_2O$

Methyl alcohol. Methyl chloride.



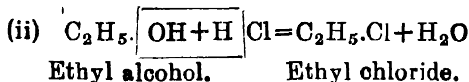
$CH_3.\boxed{OH+H}Br = CH_3.Br + H_2O$

Methyl bromide.



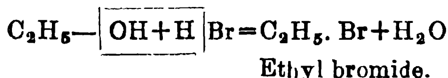
$CH_3.\boxed{OH+H}OOC.CH_3 = CH_3OOC.CH_3 + H_2O$

Acetic acid. Methyl acetate.



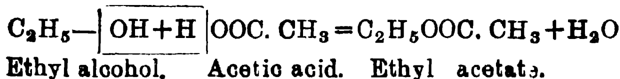
(ii) $C_2H_5.\boxed{OH+H}Cl = C_2H_5.Cl + H_2O$

Ethyl alcohol. Ethyl chloride.



$C_2H_5-\boxed{OH+H}Br = C_2H_5.Br + H_2O$

Ethyl bromide.



$C_2H_5-\boxed{OH+H}OOC.CH_3 = C_2H_5OOC.CH_3 + H_2O$

Ethyl alcohol. Acetic acid. Ethyl acetate.

The general reactions of HI and strong H_2SO_4 on alcohols.

Hydroiodic Acid acts on Alcohols in the following two stages.

(1) Esterification resulting in the formation of water and an alkyl iodide.

(2) Reduction of the alkyl iodide with the excess of hydroiodic acid.

Generel Reactions.

(i) $R-\boxed{OH+H}I = R-I + H.OH.$

Alcohol. Alkyl iodide.

(ii) $R-\boxed{I+I}H = R-H + I_2.$

Hydrocarbon.

Note :—This reaction is helpful in converting an alcohol directly into the corresponding hydrocarbon, or in replacing a hydroxyl group in any organic compound with a hydrogen atom.

The above reactions of HI are illustrated in the case of methyl and ethyl alcohols.

(i) $CH_3.\boxed{OH+H}-I = CH_3.I + H_2O$

Methyl alcohol. Methyl iodide.

(iii) $CH_3\boxed{I+I}-H = CH_4 + I_2$

Methane.

Similarly,

(i) $C_2H_5-\boxed{OH+H}-I = C_2H_5.I + H_2O$

Ethyl alcohol. Ethyl iodide.

(ii) $C_2H_5.\boxed{I+I}-H = C_2H_6 + I_2$

Ethane.

The behaviour of strong H_2SO_4 towards alcohols :—
Strong sulphuric acid acts on alcohols in three different ways, depending on different exprimental conditions. The acid acts on an alcohol forming an ester at ordinary temperature, when both the reactants are in equimolecular concentration. The ester so formed is an alkyl hydrogen sulphate, also known as sulphovinic acid. At a higher range of temperature, if the alcohol is in excess, the sulphovinic acid reacts on more of the alcohol, forming ether, on the other hand, the sulphovinic acid is decomposed, if the strong sulphuric acid is in excess, evolving an unsaturated hydrocarbon, yielding H_2SO_4 back again.

General Reactions.

The followings are the three experimentel conditions :—

I. When alcohol and the acid are in equimolecular concentration and the reaction proceeds at ordinary temperature :—

$$R-|OH+H\ HSO_4=R.HSO_4+H_2O$$

Alcohol. Sulphovinic Acid or Alkyl hydrogen sulphate.

II. When alcohol at a higher temperature is in excess, the reactions proceed in two stages :—

(i) $R-|OH+H|-HSO_4=R-HSO_4+H_2O$

Alcohol. Sulphovinic acid.

(ii) $R-|HSO_4+H|O.R=R-O-R+H_2SO_4$

Alcohol. Ether.

III. When strong sulphuric acid is in excess, the reactions proceed at a higher temperature in two stages :—

(i) $R-|OH+H|-HSO_4=R-HSO_4+H_2O$

Alcohol. Sulphovinic acid.

(ii) $R-HSO_4$ decomposes forming an unsaturated hydrocarbon and also H_2SO_4.

$R—HSO_4$ = An unsaturated hydrocarbon + H_2SO_4.

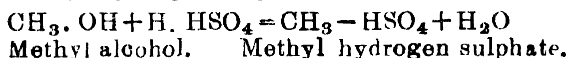
Note :—(1) The group [$—HSO_4$] of sulphovinic acid combines with one hydrogen atom of *the adjacent carbon* to form H_2SO_4, thus making one of the bonds of each of the two adjacent carbon atom free and the alcohol is changed into an unsaturated hydrocarbon.

(2) This reaction, however, go so unrepresented in the case of methyl alcohol.

The above reactions of strong H_2SO_4 are illustrated in the case of Methyl and Ethyl Alcohols.

Reactions with Methyl Alcohol.

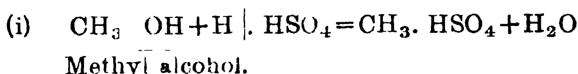
I. When methyl alcohol and strong H_2SO_4 react at ordinary temperature in equimolecular proportion, we get methyl hydrogen sulphate :—



$$CH_3.OH + H.HSO_4 = CH_3-HSO_4 + H_2O$$

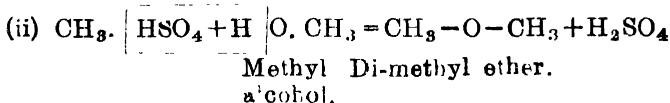
Methyl alcohol. Methyl hydrogen sulphate.

II. When methyl alcohol and strong H_2SO_4 react at a higher temperature and the former is in excess, we get di-methyl ether.



(i) $CH_3\ OH + H\ |.\ HSO_4 = CH_3.HSO_4 + H_2O$

Methyl alcohol.

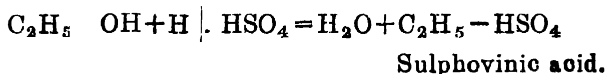


(ii) $CH_3.\ |\ HSO_4 + H\ |\ O.CH_3 = CH_3-O-CH_3 + H_2SO_4$

Methyl alcohol. Di-methyl ether.

Reactions with Ethyl Alcohol.

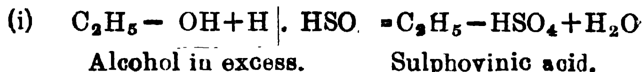
I. When ethyl alcohol acts on strong H_2SO_4 in equimolecular proportion and the reaction proceeds at 100°C, we get ethyl hydrogen sulphate or sulphovinic acid :—

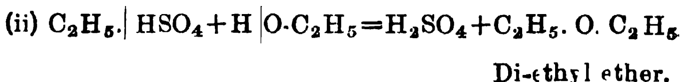


$$C_2H_5\ OH + H\ |.\ HSO_4 = H_2O + C_2H_5-HSO_4$$

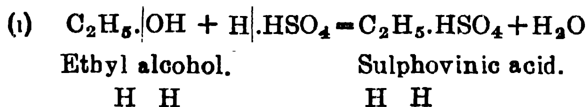
Sulphovinic acid.

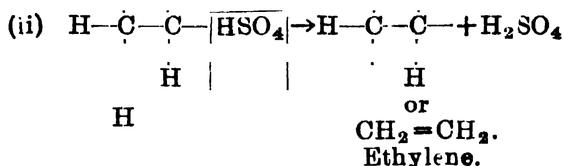
II. When ethyl alcohol acts on strong H_2SO_4 with the alcohol in excess at 140°C, we get di-ethyl ether :—


(i) $C_2H_5-OH+H|.HSO_4=C_2H_5-HSO_4+H_2O$
Alcohol in excess. Sulphovinic acid.


(ii) $C_2H_5.|HSO_4+H|O{\cdot}C_2H_5=H_2SO_4+C_2H_5.O.C_2H_5$
Di-ethyl ether.

III. When ethyl alcohol acts on strong H_2SO_4 in excess at 160°C, we get the unsaturated hydrocarbon namely ethylene :—

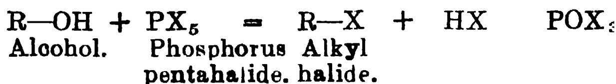

(i) $C_2H_5.|OH + H|.HSO_4=C_2H_5.HSO_4+H_2O$
Ethyl alcohol. Sulphovinic acid.


(ii) H—C(H)(H)—C(H)(H)—|HSO₄| → H—C(H)(H)—C(H)— + H_2SO_4
or
$CH_2=CH_2$.
Ethylene.

3. The general reaction of alcohols on phosphorus penta-halide.

When an alcohol acts on phosphorus penta-halide, the hydroxyl group (—OH) of the alcohol is replaced by one atom of the halogen, changing the alcohol into an alkyl halide and forming also a halogen acid along with phosphorus oxyhalide.

General Reaction.


$R—OH + PX_5 = R—X + HX \quad POX_3$
Alcohol. Phosphorus pentahalide. Alkyl halide.

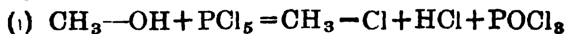
Note :—It is an important reaction used :—

(1) To replace the hydroxyl group with a halogen atom in all organic compounds.

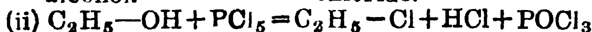
(2) To ascertain the number of hydroxyl groups in a compound, the following procedure is adopted :—

The halogen acid HX formed during this reaction is treated with silver nitrate solution. Thus the entire amount of the halogen (X) is precipitated as silver halide, which is dried and weighed. The number of the halogen atoms calculated from the weight of the silver halide will represent the number of hydroxyl groups in the compound under investigation.

The above reactions are illustrated in the case of Methyl and Ethyl Alcohols.



(i) $CH_3—OH + PCl_5 = CH_3 - Cl + HCl + POCl_3$
Methyl alcohol. — Methyl chloride.



(ii) $C_2H_5—OH + PCl_5 = C_2H_5 - Cl + HCl + POCl_3$
Ethyl alcohol. — Ethyl chloride.

(*4*) *The general reaction of alcohols on phosphorus tri-halide.*

When Alcohol acts on phosphorus tribalid three molecules of the alcohol participate in the reaction against a single molecule of the phosphorus trihalide. The hydroxyl group of the alcohol is replaced with the halogen atom, forming an alkyl halide and phosphorus acid.

General Reaction

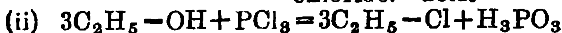


$$3R—OH + PX_3 = 3R—X + H_3PO_3$$
Alcohol. — Alkyl halide. — Phosphorus acid.

The above reactions are illustrated in the case of Methyl and Ethyl Alcohol.



(i) $3CH_3 - OH + PCl_3 = 3CH_3 - Cl + H_3PO_3$
Methyl alcohol. — Methyl chloride. — Phosphorus acid.

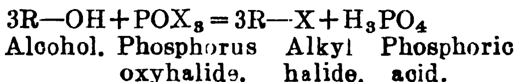


(ii) $3C_2H_5 - OH + PCl_3 = 3C_2H_5 - Cl + H_3PO_3$
Ethyl alcohol. — Ethyl chloride. — Phosphorus acid.

5. The general reactions of alcohols on phosphorus oxyhalide.

The trend of the reaction is the same as explained above. Only, we get in this case phosphoric acid instead of phosphorus acid.

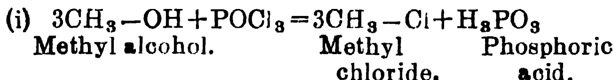
General Reaction.



$3R—OH + POX_3 = 3R—X + H_3PO_4$

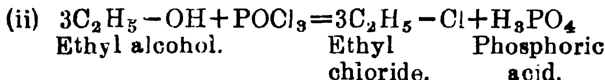
Alcohol. Phosphorus oxyhalide. Alkyl halide. Phosphoric acid.

The above reactions are illustrated in the case of Methyl and Ethyl Alcohols.



(i) $3CH_3-OH + POCl_3 = 3CH_3-Cl + H_3PO_3$

Methyl alcohol. Methyl chloride. Phosphoric acid.



(ii) $3C_2H_5-OH + POCl_3 = 3C_2H_5-Cl + H_3PO_4$

Ethyl alcohol. Ethyl chloride. Phosphoric acid.

Note :—(1) As far as these five properties of alcohols are concerned, they will hold good for primary, secondary and tertiary alcohols, because there is a common hydroxyl group (—OH) in the constitution of all the three alcohols.

[Read page 66 table 6 column No. III].

(2) With reference to page 66 and 67 the *three isomers of alochols*, can be distinguished from one another by reactions in which, their characteristic monovalent, divalent and trivalent *groups* are concerned.

Distinctive Tests of Primary, Secondary and Tertiary Alcohols.

There are two methods :—

1. Victor Meyer's method.
2. Oxidation method.

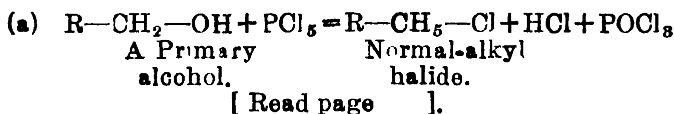
We shall consider these methods one after another.

1. VICTOR MEYER'S METHOD

Test for Primary Alcohols.

A primary alcohol having a monovalent radical [$-CH_2-OH$], when treated with phosphorus pentachloride, gives a normal-alkyl halide.

Reaction.



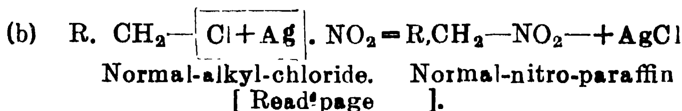
(a) $R-CH_2-OH+PCl_5=R-CH_5-Cl+HCl+POCl_3$

A Primary alcohol. Normal-alkyl halide.

[Read page].

The normal-alkyl-chloride so obtained is next treated with silver nitrite solution. The following reaction takes place and we get the corresponding normal-nitro-paraffin.

Reactton.



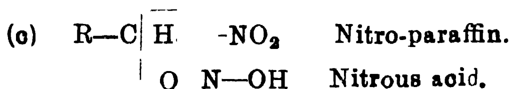
(b) $R.\ CH_2-\boxed{Cl+Ag}.\ NO_2=R,CH_2-NO_2-+AgCl$

Normal-alkyl-chloride. Normal-nitro-paraffin

[Read page].

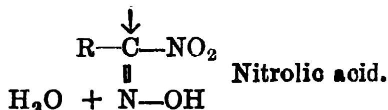
Finally, the nitro paraffin so obtained is treated with nitrous acid. The following reaction takes place forming nitrolic acid which imparts *pink* colouration to the solution, on being made alkaline.

Reaction:—



(c) $R-C|H \quad -NO_2$ Nitro-paraffin.

$\quad\quad O \quad N-OH$ Nitrous acid.



$$R-\underset{\displaystyle\|}{C}-NO_2$$

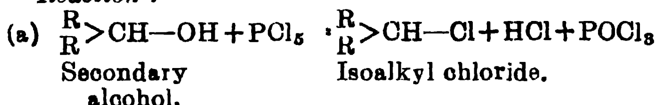
$$H_2O + N-OH$$

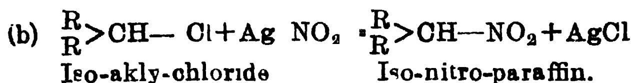
Nitrolic acid.

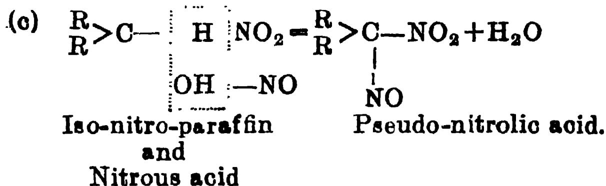
Test for Secondary Alcohols.

A secondary alcohol having a divalent radical [>CH—OH] when similarly treated forms pseudo-nitrolic acid which imparts *blue* colouration to the solution on being made alkaline.

Reaction :—



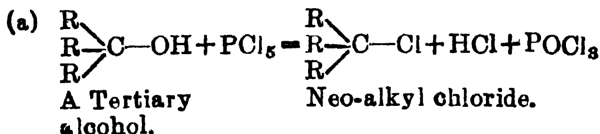


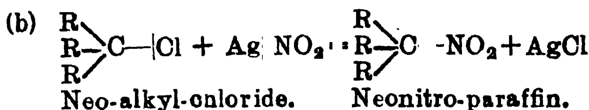


Test for Tretiary Alcohols.

A Teritary Alcohol having a trivalent radical (>C. OH) when similarly treated remains. uneffected.

Reactions :—





(c) The neo-nitro-paraffin, will have no reaction with nitrous acid and hence the solution remains colourless, on being made alkaline.

Victor Meyer's Test in a tabular form

Table No. 7

Alcohols.	Their constitution.	Treatment with PCl_5.	Treatment with $AgNO_2$ solution.	Treatment with nitrous acid (OH. NO)
1. Primary alcohol.	$R-CH_2-OH$.	$R-CH_2-Cl$ Normal alkyl chloride.	$R-CH_2-NO_2$ Normal nitro-paraffin.	A *pink* colouration when the solution is made *alkaline* with caustic soda.
2. S condary alcohol.	$\begin{matrix}R\\R\end{matrix}\!>CH-OH$.	$\begin{matrix}R\\R\end{matrix}\!>CH-Cl$. Iso-alkyl chloride.	$\begin{matrix}R\\R\end{matrix}\!>CH-NO_2$ Iso-nito-paraffin.	A *blue* colouration when the solution is made *alkaline*.
3. Tertiary alcohol.	$\begin{matrix}R\\R\\R\end{matrix}\!>C-OH$	$\begin{matrix}R\\R\\R\end{matrix}\!>C-Cl$. Neo-alkyl chloride.	$\begin{matrix}R\\R\\R\end{matrix}\!>C-NO_2$ Neo nitro-paraffin.	No reaction and hence, no colouration.

Conversion of a Primary Alcohol into the Secondary or Tertiary Alcohol.

The primary alcohol is treated with phosphorus pentachloride and we get a normal alkyl chloride.

Reaction.

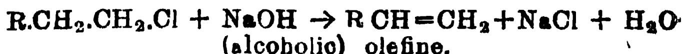


$$R.CH_2.CH_2.OH + PCl_5 \rightarrow R.CH_2.CH_2Cl + HCl + POCl_3$$

Primary alcohol. Normal alkyl chloride.

Next, the normal alkyl chloride is treated with an alcoholic NaOH solution, and we get the corresponding olefine.

Reaction

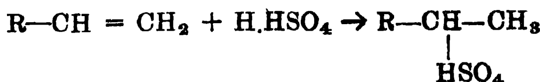


$$R.CH_2.CH_2.Cl + NaOH \rightarrow R\,CH{=}CH_2 + NaCl + H_2O$$

(alcoholic) olefine.

The olefine so obtained is made to react with fuming H_2SO_4, and we get an additive product namely an alkyl hydrogen sulphate. This additive product is formed as a rule by the addition of —HSO_4 group to that carbon atom which carries the least number of hydrogen atoms.

Reaction

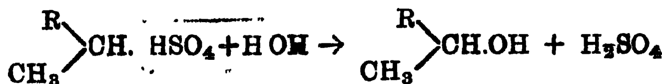


$$R{-}CH = CH_2 + H.HSO_4 \rightarrow R{-}\underset{\displaystyle HSO_4}{\underset{|}{CH}}{-}CH_3$$

olefine Alkyl hydrogen sulphate

This alkyl hydrogen sulphate on hydrolysis yields a secondary alcohol.

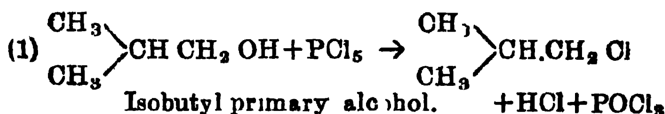
Reaction.



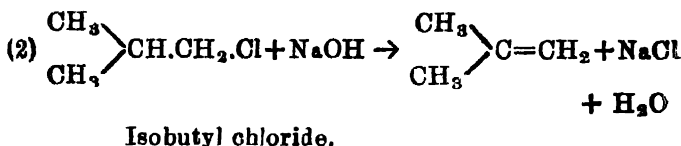
$$\begin{matrix} R \\ CH_3 \end{matrix}\!\!>CH.HSO_4 + H\,OH \rightarrow \begin{matrix} R \\ CH_3 \end{matrix}\!\!>CH.OH + H_2SO_4$$

Secondary alcohol.

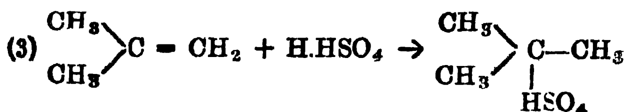
Likewise, a primary alcohol having an isoalkyl radical, as for example isobutyl primary alcohol, can be changed into a tertiary alcohol.

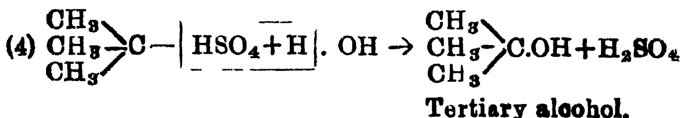


Isobutyl primary alcohol.



Isobutyl chloride.



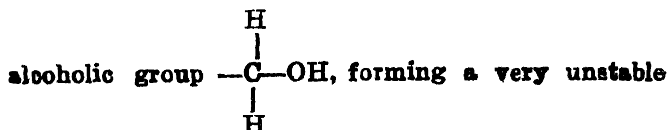


Tertiary alcohol.

2. Oxidation Method.

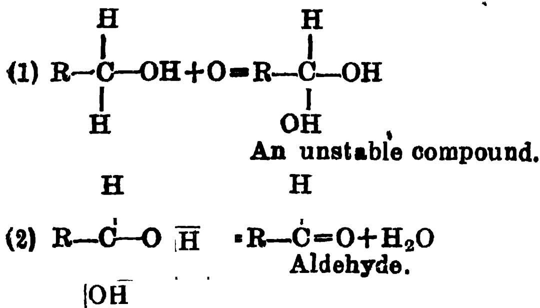
Oxidation of Primary Alcohols.

When a primary alcohol is oxidised, the oxygen atom from an oxidizing substance gets temporarily attached to one of the hydrogen atoms of the primary alcoholic group



forming a very unstable compound, which readily decomposes yielding water and a compound, commonly known as an *Aldehyde.*

General Reactions :

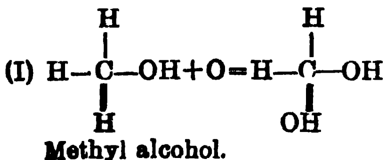


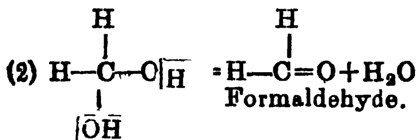
As for example.

Oxidation of Methyl and Ethyl Alcohols.

Since, both of these alcohols, have the primary alcoholic group—C(H)(H)—OH in their constitution, they behave during their oxidation as a primary alcohol.

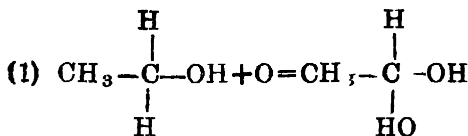
Oxidation of Methyl Alcohol.



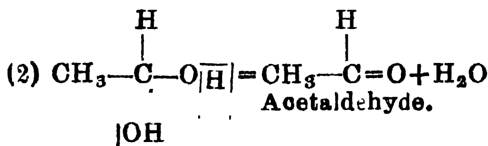


Note —Formaldehyde is the first member of the family of aldehydes. (Read chapter VI).

Oxidation of Ethyl Alcohol.



An unstable compound



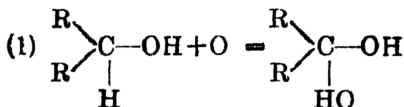
Acetaldehyde.

Note :—Acetaldehyde is the second member of the family of aldehydes.

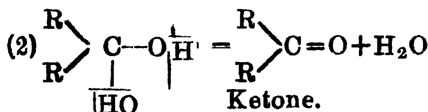
Oxidation of Secondary Alcohols.

When a secondary alcohol is oxidised, the oxygen atom from an oxidising substance gets temporarily attached to the hydrogen atom of the secondary alcoholic group >C—OH, forming an unstable compound. which readily decomposes yielding water and a compound commonly known as a *Ketone*.

General Reaction : –

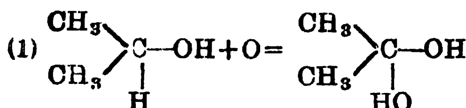


An unstable compound.

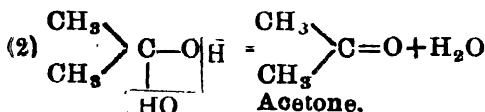


Ketone.

Oxidation of Secondary Propyl Alcohol.



Secondary propyl alcohol. An unstable compound



Acetone,

Notes 1 :—Propyl alcohol is the first alcohol which gives an example of a secondary alcohol,

2 :—Acetone is the first member of the family of ketones.

Oxidation of Tertiary Alcohols.

They differ from primary and secondary alcohols in being resistant to oxidation. Only on vigorous oxidation, they are decomposed into carbondioxide, water and a fatty acid, which has *lesser* number of carbon atoms than are originally present in the molecule of the parent alcohol.

Manufacture of Methyl Alcohol or Wood Spirit.

It is manufactured from pyroligneous acid, which is a product of destructive distillation of wood.

Destructive Distillation of Wood.

When saw dust is subjected to destructive distillation (heated in the limited supply of air) in a report R fig. 18, we obtain the following three products :—

(i A solid which is left as a residue in the retort. It is wood-charcoal.

(ii) A gas. It is wood gas which is a mixture of hydrocarbons, carbon-monoxide, and hydrogen. It is used for illuminating purposes.

(iii) A liquid distillate ; which distills ov
receiver. The distillate is a mixture of :—

(a) Wood-tar, which is a heavy, dark and thic
liquid

(b) Pyroligneous acid which is a light and brow
liquid.

The pyroligneous acid is a mixture of metnyl alcohol, acetone, acetic acid, and water. It is the source for the manufactur of methyl alcohol and acetic acid on a larg scale.

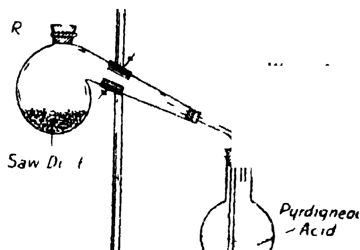


Fig 18.

Manufacturing Details of Methyl Alcohol.

Trolleys filled with wood-st cks are introduced into a chamber heated strongly by a furnace fig. 19. The gaseous product are passed through a coil condenser

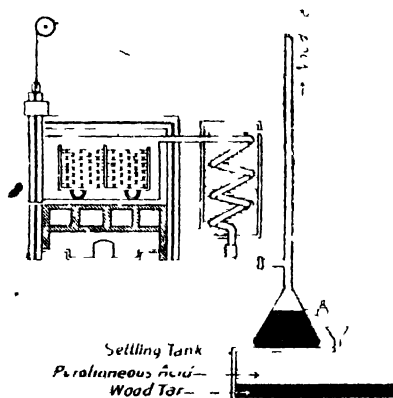


Fig. 19

submerged in cold water. The liquid distillate after condensation in the condenser collects in a settling tank and the gaseous product is led through a vertical tube as wood gas. The lower layer in the settling tank is wood-tar and the supernatant liquid is the pyroligneous acid, which is a source for obtaining methyl alcohol on commercial scale.

The pyroligneous acid so manufactured is next distilled as shown in fig. 20. The gases from the pyroligneous acid are passed through a tank containing milk of lime, which acts on acetic acid and forms calcium acetate. The vapours of methyl alcohol, acetone. and water are condensed in the condenser and collected in a tank as a distillate. The distillate in the tank is subjected to repeated *fractional distillation* (Read page 14).

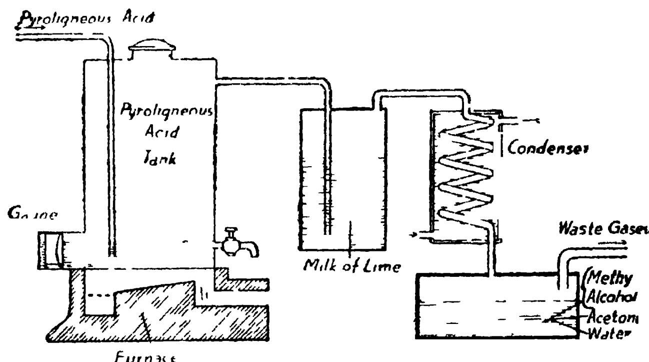


Fig. 20.

Even after repeated *fractional distillation*, methyl alcohol is not quite free from water and traces of acetone.

The methyl alcohol is dehydrated in the following way :—

The commercial methyl alcohol containing water and traces of acetone is treated with quick lime (CaO)

and kept over night. Next it is redistilled. The distillate still contains acetone in traces.

Removal of Acetone.

Anhydrous calcium chloride is added to the impure methyl alcohol. On y methyl alcohol combines with the anhydrous calcium chloride. forming a white and crystalline substance, the formula of which is $CaCl_2 . xCH_3 . OH$. On distilling this white and crystalline compound, pure methyl alcohol distills over and collects in a receiver.

Uses of Methyl Alcohol.

(1) It is used as a solvent in the manufacture of polishes, varnishes and aniline dye stuffs.

(2) Being poisonous, it is mixed with ethyl alcohol to make the latter unfit for drinking purposes.

Manufacture of Ethyl Alcohol.

It is manufactured from a "wash" a liquid, which is the product of *fermentation* of carbohydrates (sugar. glucose and starch) in solution. The "wash" contains a small percentage of ethyl alcohol, which is concentrated and purified by fractional distillation.

Fermentation.

Fermentation is a type of a chemical reaction in which organic substances undergo decomposition under the catalytic influences of *Enzymes*. which are highly complex nitrogenous, amorphous bodies of inorganic origin. The enzymes are colloidal in character and are remarkably specific in their action. A particular enzyme is capable as a rule to set up a definite chemical reaction.

A living organism like "*yeast*" in the body of which, certain enzymes are sometimes lodged, is called a *ferment*. At one time, it was believed that *fermentation* is only possible through the agency of ferments, namely ; living organisms which contain the enzymes.

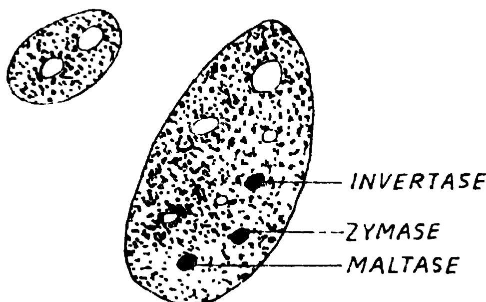
It is now exprimentally proved that the *enzymes* are capable to set up fermentations even if, they are extracted out of the living organisms namely *ferments.*

In 1896 Buckner extracted the enzymes present in the body of "yeast cells". The extract so obtained fermented the cane sugar, grape sugar solutions, and molasses exactly as "*yeast*" does.

Fermentation of cane sugar solution.

Take a dilute solution of cane sugar ($C_{12}H_{22}O_{11}$) in a flask fitted with a cork and a delivery tube, the free end of which is dipped into lime water placed in a gas jar as shown in fig. 22,

[For the manufacturing scale, fermentation is done in tanks.]



"Yeast" plants shown immensely magnified.
Fig. 21.

Add to the sugar solution a little of the unicellular, plants krown as "*yeast*" or an extract from '*yeast*". Fermentation sets in the solution after some time, if it is kept at or about 25°C in a cupboard. There will be an effervescence due to the evolution of a gas, which on examination is found to be carbon-dioxide, as it turns lime water milky. The solution left over in the flask contains very little of ethyl alcohol, which can be separated, concentrated and purified by *fractional distillation.* [Read page 14.) ?

Chemistry of Fermentation of sugar solution.

There are three *Enzymes* namely, (1) Invertase (2) Zymase and 3) Maltase usually present in the body of a "*yeast*" cell fig. 21. Each of these enzymes are capable to set up the specific chemical reaction (fermentation) characteristic of itself :—

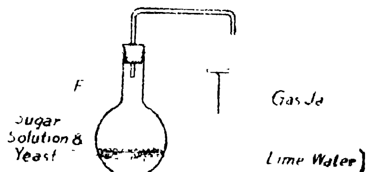
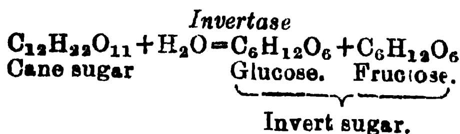


Fig. 22.

The functions of these *enzymes* are as follows :—

1. *Invertase* induces hydrolysis of cane sugar ($C_{12}H_{22}O_{11}$) in solution inverting it into a mixture of glucose and fructose. This mixture is also known as invert sugar.

Reaction.

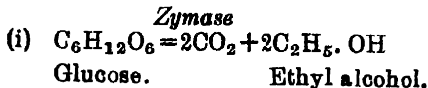


$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{\text{Invertase}} C_6H_{12}O_6 + C_6H_{12}O_6$$

Cane sugar — Glucose. Fructose. (Invert sugar.)

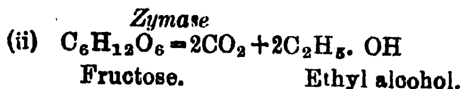
2. *Zymase* next decomposes the glucose and fructose into ethyl alcohol and carbondioxide.

Reactions.



(i) $$C_6H_{12}O_6 \xrightarrow{\text{Zymase}} 2CO_2 + 2C_2H_5.OH$$

Glucose. — Ethyl alcohol.

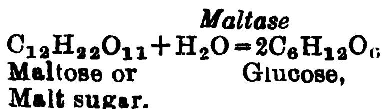


(ii) $$C_6H_{12}O_6 \xrightarrow{\text{Zymase}} 2CO_2 + 2C_2H_5.OH$$

Fructose. — Ethyl alcohol.

3. *Maltase* hydrolyses malt-sugar (maltose) into glucose.

Reaction.



$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{Maltase} 2C_6H_{12}O_6$$

Maltose or Malt sugar. Glucose,

Notes :- (1) *Maltase* does not function as an *enzyme* in the fermentation of cane sugar solution. This enzyme acts as we shall see, in the manufacture of ethyl alcohol from barley or other starchy substances, like potatoes and rice.

The fermented liquor is commercially known as "*wash*" which contains only a small percentage of ethyl alcohol.

Production of "wash" from starch contained in rice and potatoes.

Rice and potatoes are subjected to the following three processes for the production of "*wash*" :—

(1) Mashing. (2) Malting and (3) Alcoholic fermentation.

1. *Mashing* :—

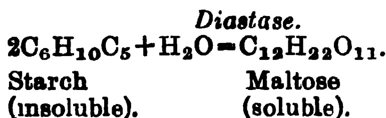
Powdered rice and potatoes are cut to thin slices and next, made into a pulp on being digested with superheated steam. During this process starch gains are liberated from the cell contents of rice and potatoes. Since starch is only sparingly soluble, it cannot be fermented by the enzymes—*Invertase* and *Zymase* —unless it is charged into a soluble form of sugar. Hence after mashing, the starchy paste is malted.

2. *Malting* :—

During this process barley grains are first made to germinate in dark. During germination, the barley grains develop an enzyme called "*Diastase*". After a few days, the further germination is stopped by heating the grains. Such germinated barley grains are

next made into a paste called "*Malt*" containing the enzyme "*Diastase*", This malt is now added to the starchy pulp obtained after mashing. The "Diastase" present in the *Malt* sets up the hydrolysis of starch which is converted into malt-sugar or maltose ($C_{12}H_{22}O_{11}$), which is a soluble and fermentable form of sugar.

Reaction.



Diastase.

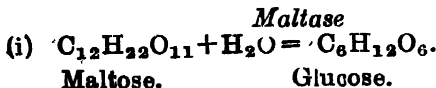
$$2C_6H_{10}C_5+H_2O=C_{12}H_{22}O_{11}.$$

Starch (insoluble). Maltose (soluble).

3. Alcoholic fermentation :—

"Yeast" or "Yeast extract" is next added to a dilute solution of maltose obtained after malting. The enzyme "maltase" present in the "yeast" hydrolyses maltose into glucose and the zymase next decomposes the glucose into carbondioxide and ethyl alcohol.

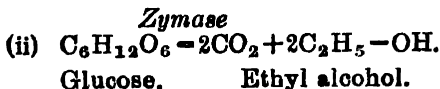
Reaction.



Maltase

(i) $C_{12}H_{22}O_{11}+H_2O=C_6H_{12}O_6.$

Maltose. Glucose.



Zymase

(ii) $C_6H_{12}O_6=2CO_2+2C_2H_5-OH.$

Glucose. Ethyl alcohol.

The fermented liquor so obtained is the "wash" containing a low percentage of ethyl alcohol along with other impurities.

.The Fractional Distillation of impure Ethyl Alcohol in Caffey's still.

Description of Caffey's still and its working.

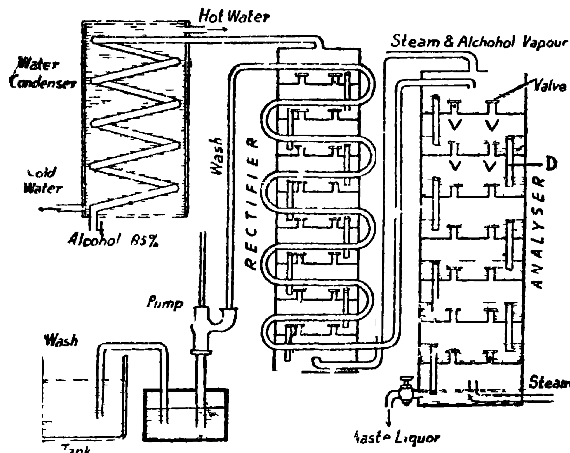


Fig. 23.

This still consists of two columns (1) an analyser and (2) a rectifier. These columns are made of wood and are lined inside with copper sheets. Both the columns are divided into a number of shelves with horizontal plates perforated with holes, which have valves (v) opening only upward. In every shelf in both the columns, there is also a drain tube D so fixed as to allow only a little layer of a liquid to remain in the shelves, making it possible for the overflow of the liquid from each shelf to be drained down into the next lower one.

Through each of the shelves in the rectifier, there passes a copper coil, whose upper end is connected with the "wash tank" through a lift pump and the lower end of the coil is carried over to the top of the analyser [See fig. 23].

The cold "wash" from the tank is pumped up through the copper coil of the rectifier to the top of the analyser. A thin layer of the "wash" collects in every shelf of the analyser. Steam is introduced into this column from the bottom. As the steam ascends, it takes vapours of ethyl alcohol more and more from shelves to shelves, as it bubbles through the thin layer of the "wash". Thus the steam, containing the maximum percentage of ethyl alcohol vapours, leaves the analyser at the top and enters the rectifier at its bottom. As the mixed vapours ascend the rectifier, most of the steam is condensed by the cool copper coil and is drained down to the bottom of the column. The vapour leaving the rectifier from the top is rich in ethyl alcohol, which is condensed in coils submerged in cold water. The distillate so obtained contains 85 % ethyl alcohol.

Rectified Spirit.

It is the alcohol collected from the rectifier of Caffey's still. The rectified spirit is an impure sample of ethyl alcohol containing aldehydes and fusel oil, which is a mixture of higher alcohols.

Pure Alcohol.

The rectified spirit is again fractionated. The distillate collected in the middle range of the temperature, is free from aldehydes and fusel oil. The sample of alcohol so obtained is pure alcohol.

Absolute Alcohol.

The pure alcohol is finally redistilled over quicklime (CaO). The distillate is absolute alcohol, still containing 5% of water which may be decomposed by metallic sodium and then it is redistilled to get absolute alcohol.

Methylated Spirit.

There is a heavy duty on pure ethyl alcohol, but when it is mixed with methyl alcohol. the methylated

spirit is rendered unfit for drinking purposes and is sold duty free. There are two forms of methylated spirit.

(*a*) *Industrial Methylated Spirit.*

It contains 95 volumes of pure alcohol and 5 volumes of crude methyl alcohol. It is used for industrial purposes.

(*b*) *Mineralised Methylated Spirit.*

It contains 90% of pure alcohol 9% methyl alcohol and 1% p troleum naptha.

Note :—The process of rendering ethyl alcohol unfit for drinking purposes by the addition of methyl alcohol is called *Denaturation.*

Uses of Ethyl Alcohol.

It is used as :—

(1) A solvent in the manufacture of paints, polishes, dyes, soaps, explosives, ether and chloroform.

(2) A fuel or as an illuminant.

(3) A beverage in wine, beer, whisky, gin, brandy, and rum.

Beverage.

Drinks containing ethyl alcohol as intoxicants are called beverages.

The following beverages are commonly in use :—

(*a*) *Wine* :—It contains a low percentage of ethyl alcohol. It is usually manufactured by the fermentation of grape sugar.

(*b*) *Beer and Whisky* :—Beer contains a low percentage and whisky 50% of ethyl alcohol. Both are obtained by fermentation of barley grains after germination.

The various beverages contain defferent colouring, flavouring, and some fragrant matter also.

Alcoholometry :—

The determination of the quantity of alcohol, present in any alcoholic liqour is called alcoholometry. "*Proof spirit*" is the standard unit adopted in alcoholometry. "*Proof Spirit*" is that alcohol which contains 49·3% volume of ethyl alcohol. In other words "Proof spirit" is that alcohol, which at 51°F or 10·5°C shall weigh $\frac{12}{13}$th of the weight of an equal volume of distilled water. The sample of alcohol having more or less percentage of this standard is "over or under *Proof Spirit*".

Test of Methyl Alcohol.

1. Oxidation Test.

Methyl Alcohol, when it is warmed with $K_2Cr_2O_7$ solution and H_2SO_4, gives formaldehyde, which can be tested by its characteristic test given later

Reactions



(a) $K_2Cr_2O_7+4H_2SO_4=K_2SO_4+Cr_2(SO_4)_3+4H_2O+3O$

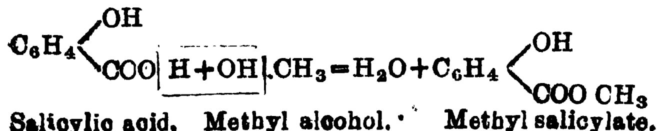


(b) $3CH_3.OH+3O=3H.CHO+3H_2O$
Methyl Alcohol. Formaldehyde.

2. Oil of Winter Green Test :—

Take a little of methyl alcohol in a test tube. Add to it a little of salicylic acid along with a few drops of strong H_2SO_4. On just warming it, methyl salicylate is produced, smelling like "oil of winter green."

Reaction.



$C_6H_4\left<\begin{matrix}OH \\ COO|H+OH|.CH_3\end{matrix}\right. = H_2O + C_6H_4\left<\begin{matrix}OH \\ COO\ CH_3\end{matrix}\right.$

Salicylic acid. Methyl alcohol. Methyl salicylate.

Test of Ethyl Alcohol.

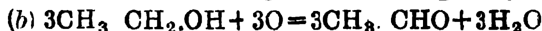
1. Oxidation Test :—

Ethyl alcohol, when warmed with $K_2Cr_2O_7$ solution and H_2SO_4, yields acetaldehyde, which can be tested by its test described later.

Reaction.



(*a*) $K_2Cr_2O_7 + 4H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3O$



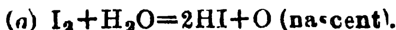
(*b*) $3CH_3\ CH_2.OH + 3O = 3CH_3.\ CHO + 3H_2O$

Ethyl alcohol　　　Acetaldehyde.

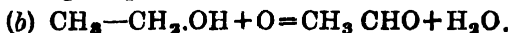
2. Iodoform Test :—

Take a little of ethyl alcohol in a test tube and add to it iodine dissolved in potassium iodide solution, till the solution is coloured dark brown. Now add to it, dilute solution of Na_2CO_3 drop by drop, till the dark brown colour is discharged. Just on warming the solution, yellow crystalls of iodoform appear, giving out its characteristic smell.

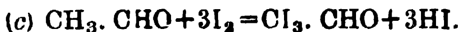
Reactions.



(*a*) $I_2 + H_2O = 2HI + O$ (nascent).



(*b*) $CH_3—CH_2.OH + O = CH_3\ CHO + H_2O$.



(*c*) $CH_3.\ CHO + 3I_2 = CI_3.\ CHO + 3HI$.

Acetaldehyde.　　　Iodal



(*d*) CI_3 | . CHO

H | . ONa

CHI_3 | H. COONa

Iodoform. | Sodium formate

Notes :—(1) Sodium carbonate, being a salt of a weak acid (H_2CO_3) and a strong base (NaOH), behaves in solution as NaOH as a result of hydrolysis as shown below :—



$$Na_2CO_3 + 2H.OH \rightarrow 2NaOH + H_2$$

(2) Acetone which is (the oxidation product of secondary propyl alcohol page 105 also gives iodoform test. But acetone will give iodoform smell, even if we add (NH_4OH) ammonium hydroxide instead of a solution of Na_2CO_3. [Ethyl alcohol fails to give iodoform test with NH_4OH. *Distinction from acetone*].

Synthesis of Methyl Alcohol

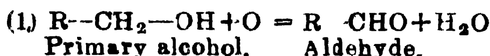
Ever since 1923, methyl alcohol is being synthesised on a large scale by *Patart process.* In this process the carbon monoxide obtained from water gas is reduced by hydrogen at 450°C and 200 atmospheric pressure in the presence of *catalysts* like zinc oxide and chromium oxide. By using different catalysts a mixture of higher alcohols can also be obtained.

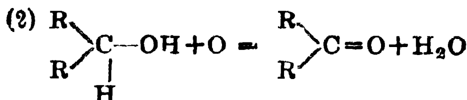
CHAPTER VI

Aldehydes and Ketones

We have learnt on pages 83 and 85 that aldehydes are the oxidation products of primary alcohols and ketones are the oxidation products of the secondary.

Reactions.





Secondary alcohol. Ketone.

General Formula of Aldehydes and Ketones.

Aldehydes = **R—CHO**

Ketones = $\genfrac{}{}{0pt}{}{R}{R}\!\!>\!C=O$

Hence,

Aldehydic group radical = [—**CHO**].

Ketonic group radical = [> **C=O**].

Graphic Formulae of the various members of Aldehydes and Ketones corresponding to the respective Alkyl Halides and Alcohols.

Table No. 8.

Serial No.	Graphic formulæ of alkyl halides.	Graphic formulæ of the members of *Alcohol* family.	Graphic formulæ of the members of *Aldehyde* family.	Graphic formulæ of the members of *Ketone* family
1.	H—CH_2—X Methyl halide.	H—CH_2—OH Methyl Alcohol	H C=O (with H below C) 1. Formaldehyde.	Nil.
2.	CH_3—CH_2—X Ethyl halide.	CH_3—CH_2—OH Ethyl Alcohol.	CH_3—C=O (with H below C) 2. Acetaldehyde.	Nil.
3.	CH_3-CH_2-CH_2—X Normal propyl halide.	CH_3—CH_2—CH_2—OH Primary propyl alcohol.	CH_3—CH_2—C=O (with H below C) 3. Propaldehyde.	Nil.

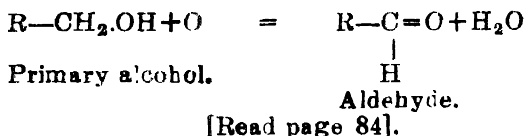
	$(CH_3)_2>C(H)-X$ Isopropyl halide	$(CH_3)_2>C(H)-OH$ Secondary propyl alcohol	Nil.	$(CH_3)_2>C=O$ Acetone. or Propanone.
4.	$C_2H_5.CH_2CH_2-X$ Normal butyl halide.	$C_2H_5-CH_2.CH_2-OH$ Primary butyl alcohol.	$C_2H_5-CH_2-C(H)=O$ Butyl Aldehyde.	Nil.
	$(C_2H_5)(CH_3)>C(H)-X$ Isobutyl halide.	$(C_2H_5)(CH_3)>C(H)-OH$ Secondary butyl alcohol.	Nil.	$(C_2H_5)(CH_3)>C=O$ Butanone or Ethyl methyl ketone.

General Methods for the Preparation of Aldehydes.

1. *The first General Method.*

It consists in oxidizing a primary alcohol with oxygen obtained from air or from a mixture of potassium dichromate and sulphuric acid.

General Reaction.



$$R—CH_2.OH + O = R—\underset{\displaystyle H}{\underset{|}{C}}=O + H_2O$$

Primary alcohol. Aldehyde.

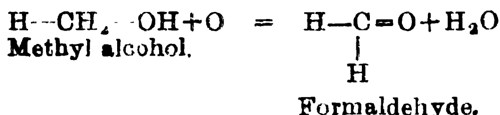
[Read page 84].

For example :—

Preparation of Formaldehyde and Acetaldehyde by the above method.

(a) By oxidizing methyl alcohol with oxygen, we can prepare formaldehyde.

Reaction.

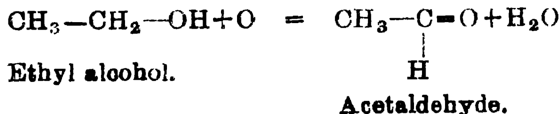


$$H—CH_2—OH + O = H—\underset{\displaystyle H}{\underset{|}{C}}=O + H_2O$$

Methyl alcohol. Formaldehyde.

(b) By oxidizing ethyl alcohol with oxygen, we can prepare acetaldehyde.

Reaction.



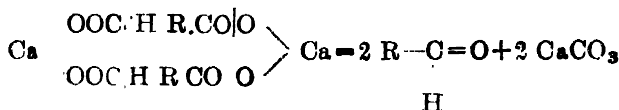
$$CH_3—CH_2—OH + O = CH_3—\underset{\displaystyle H}{\underset{|}{C}}=O + H_2O$$

Ethyl alcohol. Acetaldehyde.

2. The second General Method.

With the exception of formaldehyde, other aldehydes are prepared by distilling a mixture of calcium formate and calcium salt of a fatty acid.

General Reaction.



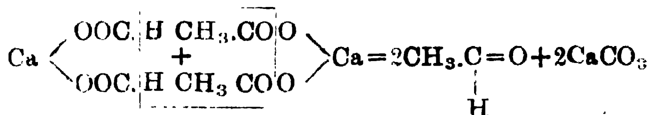
Calcium formate. Calcium salt of a fatty acid. Aldehyde.

For example :—

Preparation of Acetaldehyde by the above method.

By distilling a mixture of calcium formate and calcium acetate, we can prepare acetaldehyde.

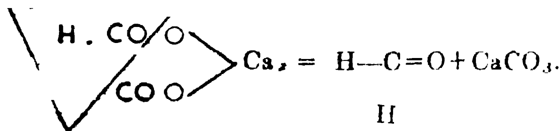
Reaction.



Calcium formate. Calcium acetate Acetaldehyde.

Preparation of Farmaldehyde

By distilling calcium formate alone, we can prepare farmaldehyde.



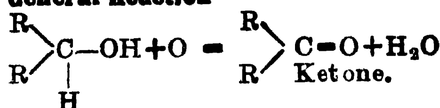
Calcium formate. Formaldehyde,

General Methods for the Preparation of Ketones.

1. *The First General Method.*

It consists in oxidizing a secondary alcohol with oxygen obtained from air or from a mixture of potassium dichromate and sulphuric acid.

General Reaction



Secondary alcohol.

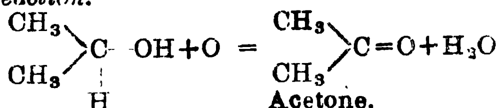
[Read page 85].

For example : –

Preparation of Acetone by the above method.

By oxidizing secondary propyl alcohol, we can prepare acetone.

Reaction.

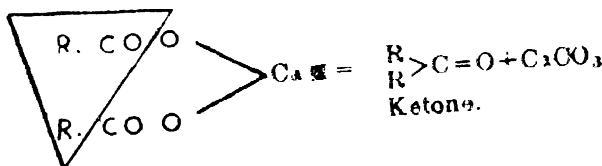


Secondary propyl alcohol.

2. *The Second General Method.*

It consists in distilling calcium salt of a fatty acid.

General Reaction.

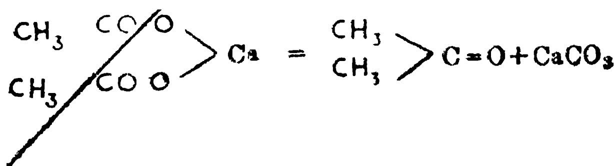


Calcium salt of a fatty acid.

Preparation of Acetone by the above method.

By distilling calcium acetate, we can prepare acetone.

Reaction.



Calcium acetate. Acetone.

General Properties of Aldehydes and Ketones.

Physical.

Aldehydes.

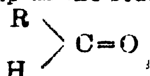
Formaldehyde is a gas. Other members of aldehydes are liquids, possessing an unpleasant and irritating smell. Their solubility decreases and boiling point increases as their molecular weight increases.

Ketones,

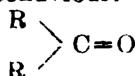
They are all liquid. They possess pleasant smell and are non-irritating.

Chemical.

The constitution of *Aldehydes* and *Ketones* are great help in the study of their chemical behaviour.



Aldehydes.



Ketones.

From the study of the above constitutions, we find that the carbonyl group [>**C=O**] enclosed by dotted lines, is common in aldehydes and ketones. The *reactions*, in which this common group takes part, will give the properties of **aldehydes** *similar* to **ketones**. Since, there is one hydrogen atom attached to the group [> C=O] in aldehydes, there are a number of *reactions*, in which *aldehydes* and *ketones* differ.

Points of Similarity between aldehydes and ketones.

1. In the *reactions*, showing similarity between aldehydes and ketones, we find, that there are the following three types of chemical changes :—

A. The *oxygen atom* attached to the carbon atom in the carbonyl group [>C=O], common between the two families, combines with H_2 of the *reactants*, liberating H_2O and the rest of the molecule of the reactants, takes up the place of oxygen in the constitution of the aldehyde and ketone.

B. The *Oxygen atom*, attached to the carbon atom in the carbonyl group [$>C<^{O-}$], common between the two families, is changed into hydroxyl (—OH) group. One of the hydrogen atoms of the *reactants* combines with the free bond of the oxygen atom and the rest of the molecule of the *reactants* gets attached to the free bond of the carbon atom in the aldehyde and ketone.

C. The *Oxygen atom* attached to the carbon atom in the carbonyl group [$>C=O$], common between the two familes, is replaced by two atoms of the halogen, with the action of phosphorus pentahalide.

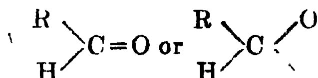
General Properties showing similarity between Aldehydes and Ketones in table No 9.

[In the table the properties of aldehydes and ketones are dealt with on the left and right hand pages respectively].

Table

Aldehydes.

General Constitution.

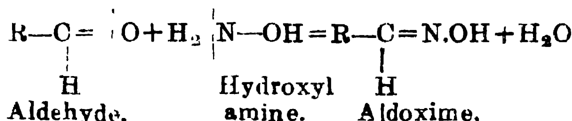


(A) *Reactions in which the* **Oxygen atom** *in the carbonyl group* [>C=O] *is removed as* H_2O.

There are three such reactions :—

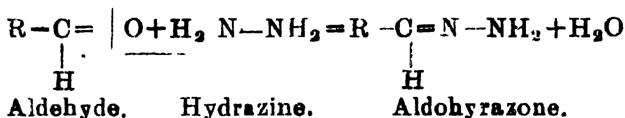
1. When aldehydes act on hydroxyl amine [H_2N OH], we get water and a compound called aldoxime.

General Reaction.



2. When aldehydes act on hydrazine [$H_2N—NH_2$], we get water and a compound called aldohydrazone.

General Reaction.

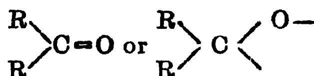


3. When aldehydes act on phenyl hydrazine, we get water and aldo-phenylhydrazone.

No. 9.

Ketones.

General Constitution.

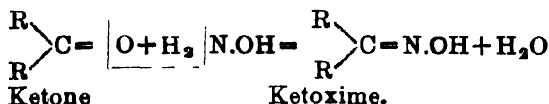


(*A*) *Reactions in which the* **Oxygen atom** *of the carbonyl group* [> *C*=*O*], *is removed as* H_2O.

There are three such reactions :--

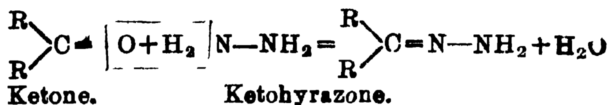
1. When ketones act on hydroxyl amine [$H_2N—OH$], we get water and a compound called ketoxime.

General Reaction.



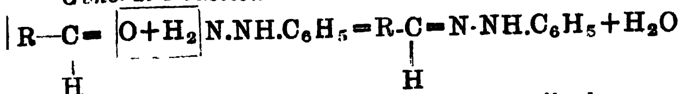
2. When ketones act on hydrazine [$H_2N\text{-}NH_2$], we get water and a compound called ketohydrazone.

General Reaction.



3. When ketones act on phenyl hydrazine, we get water and keto-phenylhydrazone.

General Reaction.



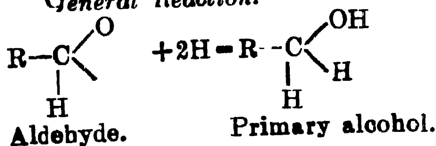
Aldehyde. Phenyl hydrazine. Aldo-phenylhydrazone.

B. Reactions in which the oxygen atom of the group [>C<O—] *, is changed into hydroxyl* (—OH) *group* :-

There are also three such reactions :—

4. When aldehydes are reduced by *nascent* hydrogen, we get a compound called primary alcohol.

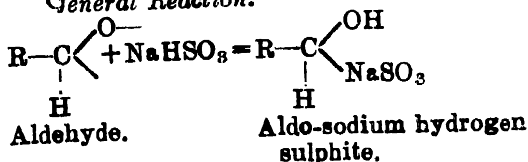
General Reaction.



Aldehyde. Primary alcohol.

5. When aldehydes act on sodium hydrogen sulphite, we get aldo-sodium hydrogen sulphite.

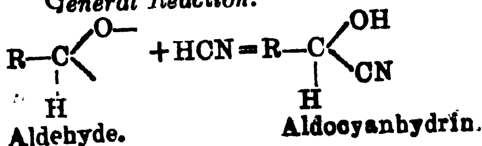
General Reaction.



Aldehyde. Aldo-sodium hydrogen sulphite.

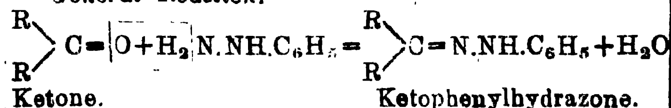
6. When aldehydes act on hydrocyanic acid, we get a compound called aldo-cyanhydrin.

General Reaction.



Aldehyde. Aldocyanhydrin.

General Reaction.



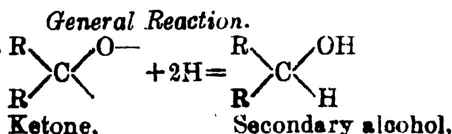
Ketone. Ketophenylhydrazone.

B. Reaction in which the oxygen atom of the carbonyl group [$>C<^{O-}$], *is changed into hydroxyl (—OH) group :—*

There are also three such reactions :—

4. When ketones are reduced by *nascent* hydrogen, we get a compound called secondary alcohol.

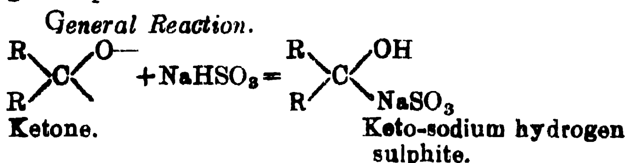
General Reaction.



Ketone, Secondary alcohol,

5. When ketones act on sodium hydrogen sulphite, we get a compound called keto-sodium hydrogen sulphite.

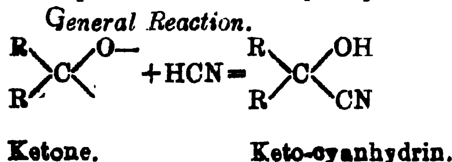
General Reaction.



Ketone. Keto-sodium hydrogen sulphite.

6. When ketone act on hydrocyanic acid, we get a compound called keto-cyanhydrin.

General Reaction.

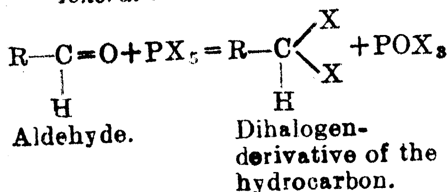


Ketone. Keto-cyanhydrin.

C. The reaction, in which the **oxygen atom** *of the carbonyl group [$>C=O$] is replaced by a halogen.*

7. **When aldehydes are treated with phosphorus-penta halide, we get the dihalogen-derivative of the corresponding hydrocarbon and phosphorus oxy-halide.**

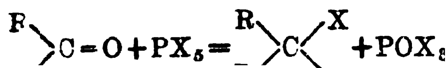
General Reaction.



C. The reaction in which the **oxygen atom** *of the carbonyl group [>C=O] is replaced by a halogen.*

7. When ketones are treated with phosphorus-penta-halide, we get the dihalogen-derivative of the corresponding hyrocarbon and phosphorus-oxyhalid

General Reaction.



derivative of
hydrocarbon.

The above **seven** *points of similarity between the the first two members of the aldehyde*

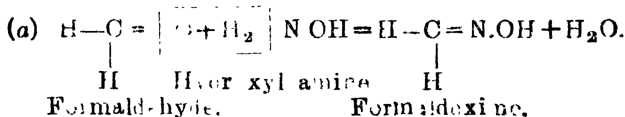
Table

Members	Aldehydes.
First	Formaldehyde H—C=O (with H below C)
Second	Acetaldehyde CH_3—C=O (with H below C)

A. The three reactions involving the removal of the oxygen atom as H_2O.

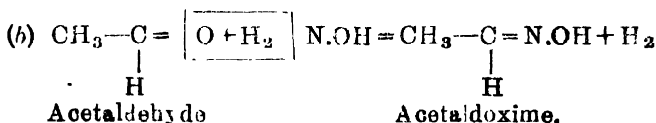
1. *Formaldehyde* acts on hydroxyl amine forming water and form aldoxime. *Acetaldehyde* treated likewise yields acetaldoxime.

Reaction.



(a) $H—C(H)=[O+H_2]N.OH = H—C(H)=N.OH + H_2O.$

Formaldehyde. Hydroxyl amine. Formaldoxime.



(b) $CH_3—C(H)=[O+H_2]N.OH = CH_3—C(H)=N.OH + H_2O$

Acetaldehyde Acetaldoxime.

2. *Formaldehyde* acts on hydrazine forming water and formaldohydrazone. *Acetaldehyde* treated likewise yields acetaldohydrazone.

two families is given in the table No: 10 *as illustrated by and only the first of the ketone.*

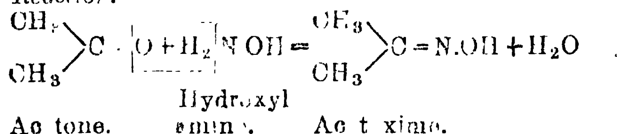
No. 10.

Member.	Ketone.
First.	Acetone $\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>C=O$

A. The three reactions involving the removal of the oxygen atom as H_2O.

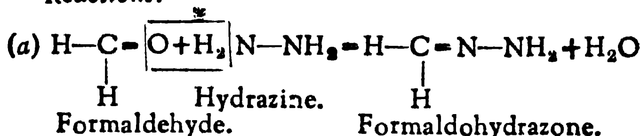
1. *Acetone* acts on hydroxyl amine forming water and ketoxime.

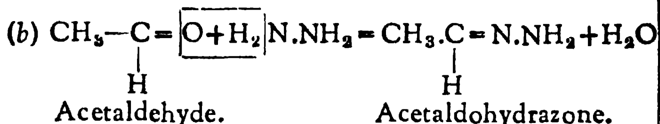
Reaction.



2. *Acetone* acts on hydrazine forming water and acetohydrazone.

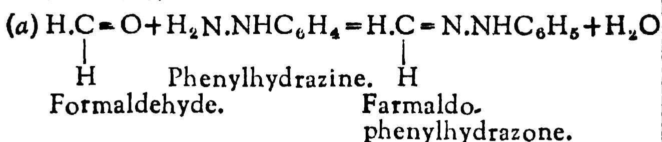
Reactions.

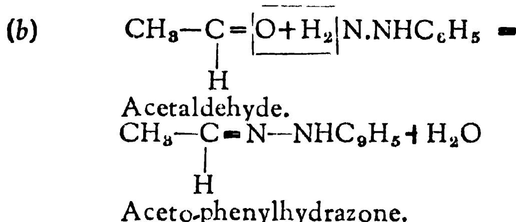




3. *Formaldehyde* acts on phenylhydrazine forming water and formaldo-phenylhydrazone. *Acetaldehyde* treated like-wise yields acetaldo-phenylhydrazone.

Reactions.

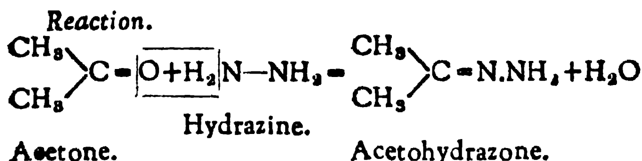




B. *The three reactions involving the change of the oxygen atom into hydroxyl group (— OH).*

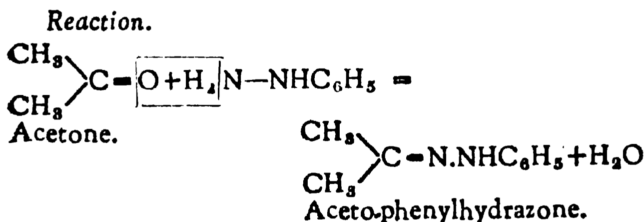
4. *Formaldehyde,* when reduced by *nascent* hydrogen, gives methyl alcohol. *Acetaldehyde* treated like-wise will yield ethyl alcohol.

Reaction.



3. *Acetone* acts on phenylhydrazine forming water and aceto-phenylhydrazone.

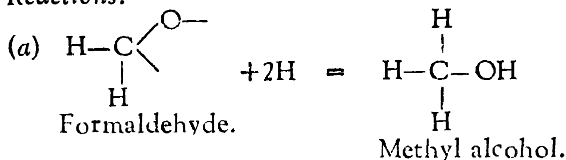
Reaction.

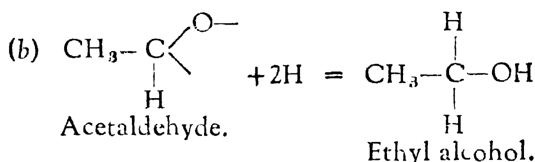


B. *The three reactions involving the change of the oxygen atom into hydroxyl group (—OH).*

4. *Acetone*, when reduced by *nascent* hydrogen, gives secondary propyl alcohol.

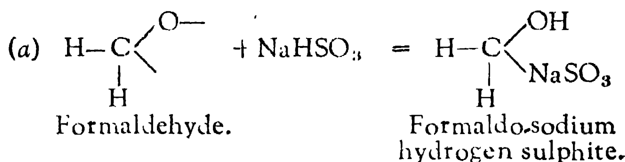
Reactions.

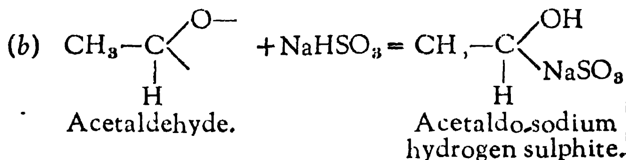




5. *Formaldehyde*, when acts on a solution of sodium hydrogen sulphite, gives formaldo-sodium hydrogen sulphite. *Acetaldehyde* treated like-wise yields acetaldo-sodium hydrogen sulphite.

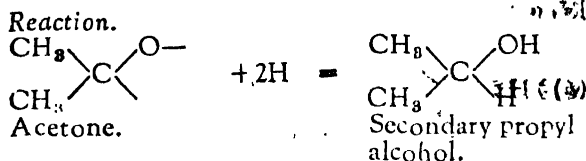
Reactions.





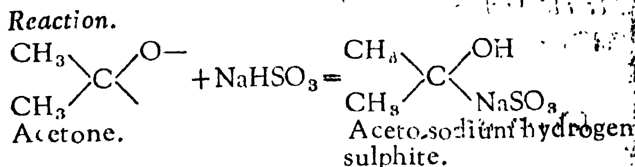
6. *Formaldehyde*, when acts on hydrocyanic acid, gives formaldocyan-hydrin. *Acetaldehyde* treated like-wise yields acetaldocyanhydrin.

Reaction.



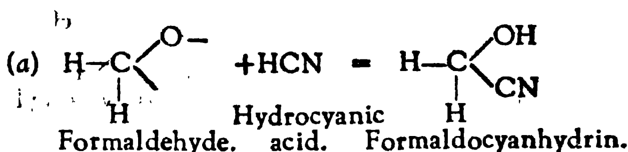
5. *Acetone*, when acts on a solution of sodium hydrogen sulphite, gives aceto-sodium hydrogen sulphite.

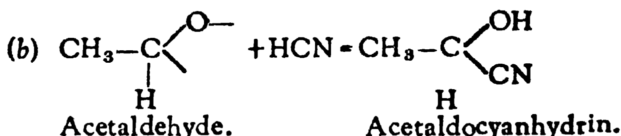
Reaction.



6. *Acetone*, when acts on hydrocyanic acid, gives acetocyanhydrin.

Reactions.

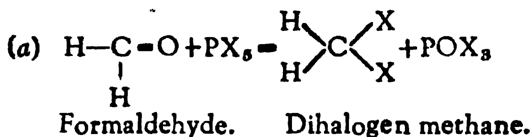


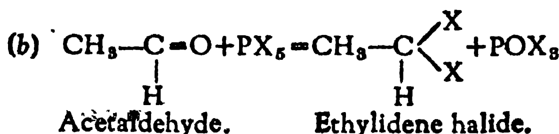


C. *The reaction involving replacement of the oxygen atom by two atoms of a halogen.*

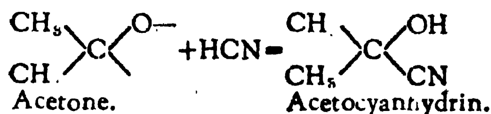
7. *Formaldehyde*, when reacts with phosphorus penta-halide, gives dihalogen derivative of methane, *Acetaldehyde* treated like-wise yields ethylidene halide.

Reactions.





Reaction.

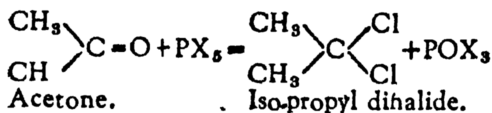


Acetone. Acetocyanhydrin.

C. *The reaction involving replacement of the oxygen atom by two atoms of a halogen.*

7. Acetone, when reacts with phosphorus penta-halide, gives iso-propyl-dihalide.

Reaction.



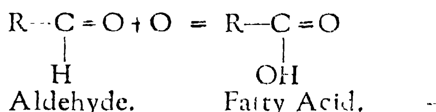
Acetone. Iso-propyl dihalide.

Since one hydrogen atom is attached to the carbonyl group (>C=O) in the constitution of an aldehyde, there are a number of *reactions*, in which aldehydes *differ* from ketones.

The following are the points in which **Aldehydes** *differ* from **Ketones**.

(1) *Aldehydes* are *easily* oxidised even by weak oxidising substances, forming fatty acids retaining the ***same number*** of carbon atoms as are originally present in a molecule of the aldehyde.

General Reaction.



Ketones are *not easily* oxidised. If, however, they are treated with strong oxidising substances, they are slowly decomposed into water, carbon-dioxide and a fatty acid which have *lesser* ***number*** of carbon atoms, than are originally present in a molecule of the ketone.

(2) *Aldehydes* are strong reducing agents. Any organic compound, having an aldehydic group (– CHO), will be able to behave as a reducing agent. As such they are able to reduce : –

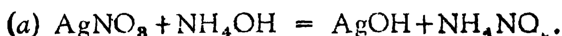
(*a*) An ammonical solution of silver nitrate to metallic silver.

(*b*) Fehling's solution to a red precipitate of cuprous oxide.

Experiments to illustrate the properties of aldehydes as reducing agents.

(*a*) Prepare a dilute solution of $AgNO_3$ in distilled water. Add to it ammonium hydroxide, till a brown precipitate of silver hydroxide is formed. Continue adding more of ammonium hydroxide ***drop by drop***, till the precipitate first formed, is *just* redissolved.

Reactions.



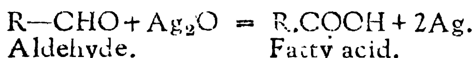
(*a*) $AgNO_3 + NH_4OH = AgOH + NH_4NO_3$.



(*b*) $2AgOH = Ag_2O \cdot H_2O$.

Thus the ammoniacal solution of $AgNO_3$ contains Ag_2O. Add a little of an aldehyde to this solution. The aldehyde will be able to reduce Ag_2O to metallic silver.

General Reaction.



$R{-}CHO + Ag_2O = R.COOH + 2Ag$.
Aldehyde. Fatty acid.

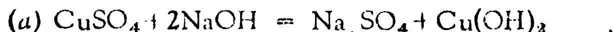
(*b*) Prepare Fehling's solution, which is a mixture of solutions No: A and No: B.

Solution No: A is prepared by dissolving 4 gms. of $CuSO_4$ in 10 gms. of distilled water.

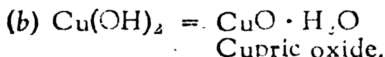
Solution No: B is prepared by dissolving 8 gms. of NaOH and 20 gms. of Rochelle salt (sodium potassium tartarate) in 60 c.c. of distilled water.

Solution No: A and No: B taken in equal volumes is the Fehling's solution.

Reactions.



(*a*) $CuSO_4 + 2NaOH = Na_2SO_4 + Cu(OH)_2$

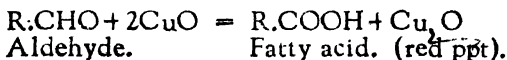


(*b*) $Cu(OH)_2 = CuO \cdot H_2O$
Cupric oxide.

The cupric oxide (CuO), so formed remains dissolved in Rochelle salt solution.

The Fehling's solution containing cupric oxide, when added to a little of an aldehyde, is reduced to cuprous oxide (Cu_2O), which is precipitated in red colour.

General Reaction.



$R.CHO + 2CuO = R.COOH + Cu_2O$
Aldehyde. Fatty acid. (red ppt).

Ketones are *not* able to behave as reducing agents.

(3) *Aldehydes* develope a violet red colour, when a little of it is added to an aqueous solution of Rosaniline (magenta or fuchsine) decolourised by SO_2 gas. This test is a sensitive test for aldehydes and is better known as *Schiff's Test*, after the name of the Professor of the Turin University of Italy.

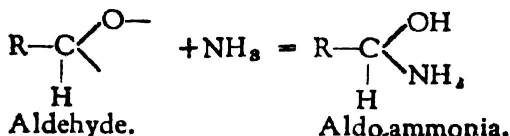
Ketones do not give *Schiff's Test.*

(4) *Aldehydes with the exception of formaldehyde,* when boiled with a fairly strong solution of caustic soda, form resin—a brown substance of complex constitution. Formaldehyde similarly treated, yields methyl alcohol and sodium formate.

Ketones do not react with caustic soda solution.

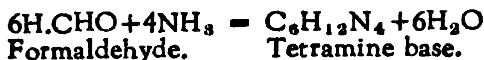
(5) With the exception of formaldehyde, other *aldehydes* act on *dry* ammonia forming aldo-ammonia.

General Reaction.



Formaldehyde does not give formaldo-ammonia with dry ammonia. It acts on ammonia yielding water and hexamethylene tetramine base.

Reaction.



$$6H.CHO + 4NH_3 = C_6H_{12}N_4 + 6H_2O$$

Formaldehyde. Tetramine base.

Ketones do not act on ammonia.

(6) *Aldehydes* undergo polymerisation as well as condensation.

Ketones do not polymerise, they undergo only condensation.

Polymerisation.

It is a reversible chemical change, in which two or more molecules of an organic compound, unite to form a product, whose molecular weight is a multiple of the molecular weight of the original compound.

Note :—The unstability of the products produced during polymerisation, is due to the fact, that such products are formed by the union of the molecules generally through the bond of *oxygen* atom.

Ketones although do not polymerise, yet undergo slightly a different kind of chemical change, called *condensation.*

Condensation.

It is an irreversible chemical change, in which two or more molecules of the same or different compounds unite through *only* the bonds of a *carbon* atom, to form a more complex and stable compound with or without liberating H_2O or HCl molecules.

Note :—The stability of the compounds formed during condensation is probably due to the fact, that such compounds are formed by the union of the molecules through the bonds of a carbon atom.

The above **six** *points of dis-similarity between the two families are illustrated by the first two members of the aldehydes and only* **the first** *of the ketones in the table No.* 11.

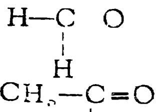
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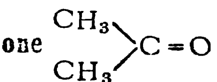
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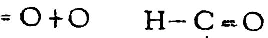
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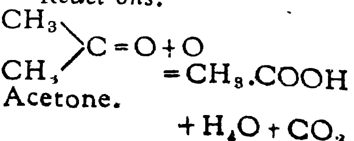
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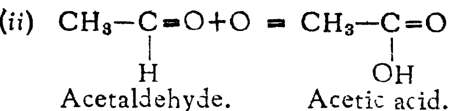
Acetone is not easily oxidised. Only powerful oxidising agents, do slowly oxidise it in o water and compounds which have *lesser number of carbon atoms*, than are present in the molecules of acetones.

Reactions.



$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>C=O+O = CH_3.COOH + H_4O + CO_2$$

Acetone.



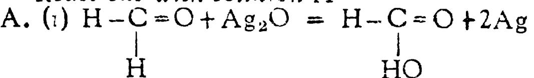
(*ii*) $CH_3-C(H)=O + O = CH_3-C(OH)=O$

Acetaldehyde. Acetic acid.

2. *Formaldehyde* and *Acetaldehyde* behave as strong reducing agents towards :—

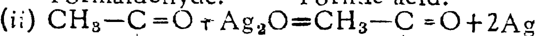
(A) an ammonical solution of silver nitrate and (B) a Fehling's solution reducing both the above solutions to metallic silver and a red precipitate of cuprous oxide respectively.

Reactions with solution A :—



A. (i) $H-C(H)=O + Ag_2O = H-C(HO)=O + 2Ag$

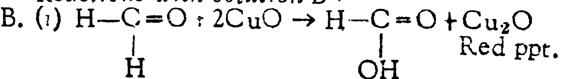
Formaldehyde. Formic acid.



(ii) $CH_3-C(H)=O + Ag_2O = CH_3-C(HO)=O + 2Ag$

Acetaldehyde. Acetic acid.

Reactions with solution B :—



B. (i) $H-C(H)=O + 2CuO \rightarrow H-C(OH)=O + Cu_2O$

Red ppt.

Formaldehyde. Formic acid.

Acetone is not a reducing agent. It is not able to reduce either an ammonical solution of silver nitrate or Fehling's soluion.

Serial No.	**Aldehydes.**	**Ketones**
	(*ii*) $CH_3—\underset{\mid \atop H}{C}=O+2CuO=CH_3-\underset{\mid \atop HO}{C}=O+Cu_2O$ red ppt. Acetaldehyde. Acetic acid.	
3.	*Formaldehyde* and *Acetaldehyde* develop a violet-red colour, when they are added to the solution of Rosaniline after being decolourised by sulphur dioxide. Both of them will respond to this sensitive test, which is known as *Schiff's Test*.	*Acetone* does not respond to *Schiff's Test*.
4.	*Acetaldehyde*, when boiled with a fairly strong solution of caustic soda yields resin—a brown substance of complex constitution. *Formaldehyde*, however, does not form resin. when it is treated with caustic soda solution. but gives methyl alcohol and sodium formate. *Reaction.* $2H—CHO+NaOH \rightarrow CH_3.OH+H.COONa$ Formaldehyde. Methyl alcohol.	*Acetone* is without any action on a solution of caustic soda.

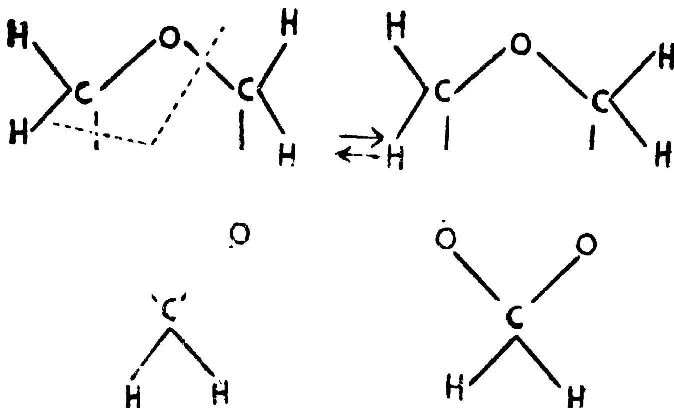
5.	*Acetaldehyde* like other aldehydes, when treated with *dry* ammonia forms acetaldo-ammonia. *Formaldehyde,* however, treated like-wise yields *hexamethylene tetramine base.* *Reactions.* (*i*) $CH_3-\overset{\displaystyle H}{\underset{}{C}}\langle^{O-}$ $+ NH_3 = CH_3-C\langle^{O-H}_{NH_2}$ (with H below C) Acetaldehyde. Acetaldo ammonia. (*ii*) $6H-CHO + 4NH_3 = C_6H_{12}N_4 + 6H_2O$ Formaldehyde. Hexamethylene tetra-mine base.	*Acetone* does not act on ammonia.
6.	*Formaldehyde* and *Acetaldehyde* undergo *polymerisation.* Reactions examplifying polymerisation of aldehydes is given at the end of this table.	*Acetone* does not *poly-merise;* but, it does undergo *condensation.* Reactions during condensation of acetone is given at the end of this table.

Example of polymerisation of aldehydes :—

1. Three molecules of formaldehyde polymerise to form trioxymethylene, whose molecular weight is triple that of the formaldehyde.

Reaction.

Formaldehyde. Trioxymethylene.



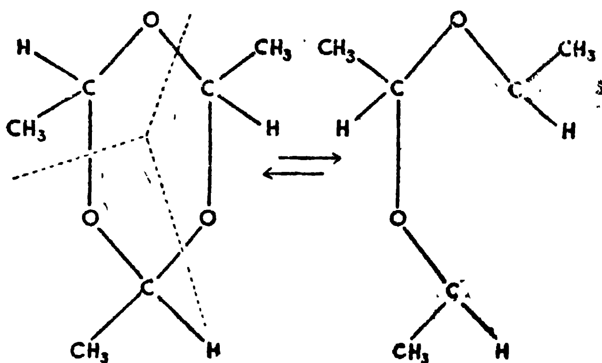
Three molecules. A single molecule.

Trioxymethylene is formed when formaldehyde is treated with a little of dilute acids or alkalis.

2. Three molecules of acetaldehyde polymerise to form *paraldehyde* whose molecular weight is triple that of the acetaldehyde.

Paraldehyde is formed when acetaldehyde is treated with a little dilute acids or alkalis.

Reaction.

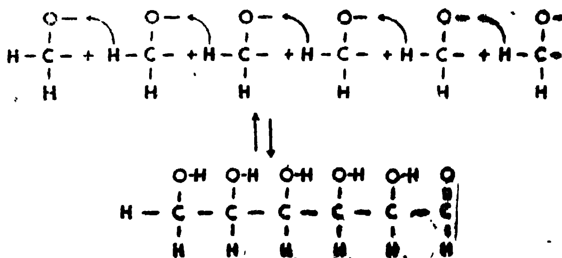


Three molecules. A single molecule.

Examples of condensation of aldehydes :—

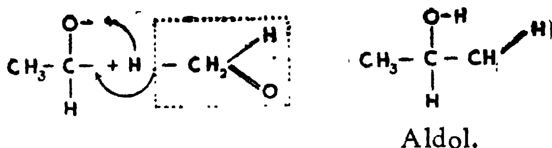
1. Six molecules of formaldehyde condense to form glucose or fructose, whose molecular weight is a multiple of that of formaldehyde. It is a very important reaction taking place in the green plant leaves under the influence of the radiant energy from the sun.

Reaction.



2. Two molecules of acetaldehyde are condensed to form **Aldol**, when treated with a solution of potassium carbonate. (*Aldol condensation*).

Reaction.



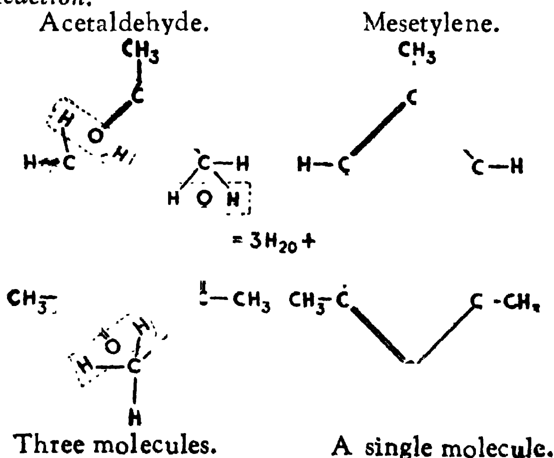
Aldol.

Examples of condensation of ketones :—

We have already met with at least three examples of condensation, while studying the behaviour of (1) hydroxylamine, (2) hydrazine and (3) phenylhydrazine towards ketones. (Refer to table No. 9, pages 109 and 111). In all these reactions, the molecular combination is effected through the *carbon linkage*, liberating water and a condensation product. Hence these reactions are irreversible and the condensation products are stable.

Apart from the above examples of condensations, acetaldehyde when treated with concentrated sulphuric acid and fractionated, yields mesetylene as a distillate.

Reaction.



Three molecules.

A single molecule.

Laboratory method for the preparation of formaldehyde.

It consists in oxidising methyl alcohol vapour with the atmospheric oxygen, in the presence of heated copper wire gauze which acts as a catalyst.

About 60 c. c. of methyl alcohol are taken in a conical flask, which is fitted up with an inlet tube reaching right up to the bottom of the flask and also with an outlet tube, connected to one end of a combustion tube containing a copper wire gauze. The other end of the combustion tube is connected with another conical flask containing a little water. The exit tube A of this flask is attached to a suction

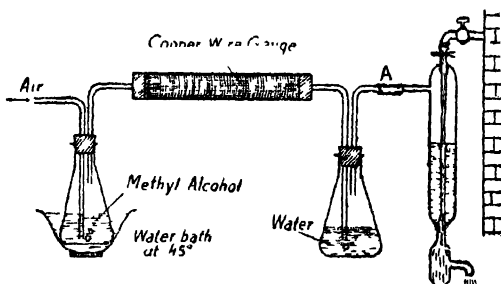
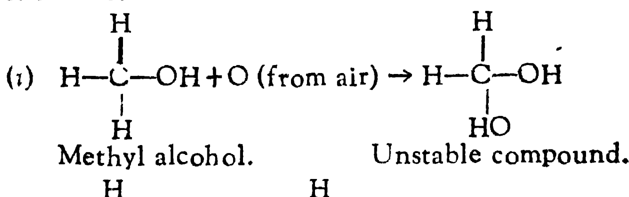


Fig. 24.

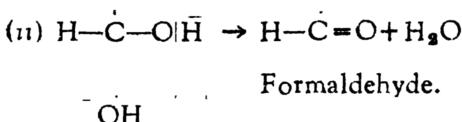
pump as shown in fig. 24. The conical flask, containing methyl alcohol is heated over water bath at 45°C (the heating arrangement is not shown in the figure). As the flask is being heated, the exhaust pump is made to suck air through methyl alcohol taken in the conical flask. The methyl alcohol vapour mixed with atmospheric oxygen is passed through the heated copper wire gauze kept in the combustion tube. The methyl alcohol is oxidised by the atmospheric oxygen to formaldehyde—copper wire gauze acting as a catalyst.

Reactions.



(i) H—C(H)(H)—OH + O (from air) → H—C(H)(OH)—OH

Methyl alcohol. Unstable compound.



(ii) H—C(H)(OH)—O|H → H—C(H)=O + H_2O

Formaldehyde.

The formaldehyde vapour is dissolve in water taken in the conical flask shown at the right hand of the Fig. No: 24. Formaldehyde is always prepared and commercially sold as an aqueous solution. **Formaline** is a commercial name given to an aqueous solution of 40% formaldehyde.

Properties of formaldehyde.

Physical.

It is a colourless gas, possessing a characteristic irritating smell. It is fairly soluble in water.

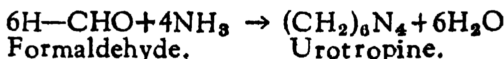
Chemical.

(Read table No: 10, pages 114, 116, 118 and 120 and also table No: 11, pages 126 to 129).

The following are the points in which *formaldehyde differs from other aldehydes* :—

(1) Formaldehyde, when treated with *dry* ammonia, does not form aldo-ammonia; but, it yields a white and crystalline solid called hexamethylene tetramine base used in medicine as "Urotropine".

Reaction.



$$6H\text{—}CHO + 4NH_3 \rightarrow (CH_2)_6N_4 + 6H_2O$$

Formaldehyde. Urotropine.

(2) Formaldehyde, on being boiled with a strong solution of caustic soda, does not form resin; but yields methyl alcohol and sodium formate.

Reaction.

$$2H-CHO + Na.HO \rightarrow CH_3-OH = H.COONa$$

Formaldehyde. Methyl alcohol. Sodium formate.

Sensitive test for formaldehyde.

Remine's Test.

It is a sensitive test used to detect the presence of formaldehyde. The following is the procedure for performing this test :—

Take two or three drops of phenylhydrazine in a test tube nearly half-ful of water. Acidify it with dilute HCl to obtain a solution of phenylhydrazine hydrochloride ($C_6H_5-NH-NH_2.HCl$).

Take about one c. c. of this acidified solution into a test tube. Add to it about 2 c. c. of formaldehyde solution. Introduce NaOH in excess, till the solution is definitely alkaline. *Formaldehyde* developes an intensely *blue* colour whereas *acetaldehyde*, similarly treated developes *deep red* colour.

Note :—None of these colours is, however permanent. The colours fade away after sometime.

Uses of formaldehyde.

Formaldehyde is *commercially* known as *formaline* and it is used :—

(1) as a preservative for biological specimens,

(2) as a fixitive of gelatine films on photographic plates,

(3) as an antiseptic and disinfectant,

(4) in the manufacture of "bakalite" a substitute for "ivory". Bakalite is a condensation product of formaldehyde and phenol, and also

(5) in the manufacture of dyes and drugs.

Laboratory method for the preparation of acetaldehyde.

It consists in oxidising ethyl alcohol by an oxidising solution, which is prepared by dissolving potassium dichromate ($K_2Cr_2O_7$) in water along with sulphuric acid.

A solution of 25 grams of $K_2Cr_2O_7$ dissolved in 100 c. c. of water is taken in a distilling flask, fitted up with a tap-funnel and a condenser connected to a receiver, which is kept in a basin containing a freezing mixture. The condenser and the flask are clamped suitably to a stand. The distilling flask is supported over a water bath. A mixture of 50 c. c. of ethyl alcohol and 20 c. c. of strong H_2SO_4 is taken in the dropping funnel. (Refer to fig. 25).

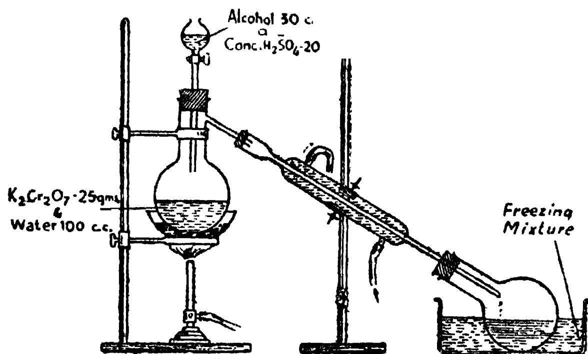
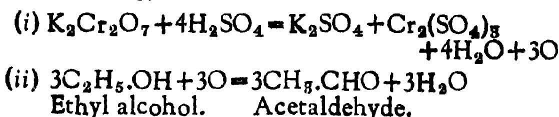


Fig. 25.

The liquid in the distilling flask is warmed over the water bath. The alcoholic mixture from the tap-funnel is introduced into the flask a little by little. As ethyl alcohol is oxidised, the potassium dichromate solution turns green. Since the alcoholic oxidation is a strongly exothermic reaction, the green solution in the distilling flask soon begins to boil.

The flame is thereafter removed. The liquid from the tap-funnel is introduced into the flask at the rate at which the distillate collects in the receiver. The distillate in the receiver, is an impure sample of acetaldehyde. Ethyl alcohol, ether, sulphurous acid and water are the chief impurities.

Reaciions.



(*i*) $K_2Cr_2O_7 + 4H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3O$

(*ii*) $3C_2H_5.OH + 3O = 3CH_3.CHO + 3H_2O$
Ethyl alcohol. Acetaldehyde.

Purification of acetaldehyde.

The distillate as obtained above in the receiver is taken in a flask, fitted up with a reflex condenser, the upper end of which is connected by a long vertical bent tube to the two conical flasks, each containing about 100 c.c. of ether as shown in Fig. 26.

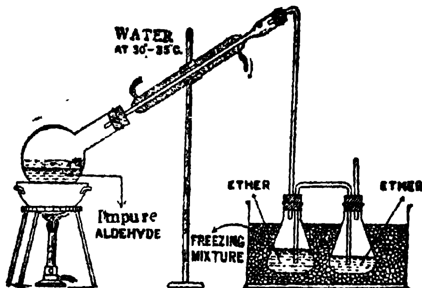


Fig. 26.

The flask containing the impure sample of acetal-dehyde is heated over sand bath along with a few glass beads which prevent bumping of the liquid in the flask. Water between 30°C and 35°C is kept in circulation through the reflex condenser. Between this range of temperature, only pure acetaldehyde does not condense, whereas, water and ethyl alcohol

are condensed and reflexed back into the flask. The vapour of acetaldehyde dissolves in ether placed in the two conical flasks, and we get an ethereal solution of acetaldehyde. The solution so obtained is next saturated with *dry ammonia*, which combines with acetaldehyde to form acetaldo-ammonia, the solution of which is next cooled by a freezing mixture. The acetaldo-ammonia crystallises out, as the solution cools. The acetaldo-ammonia so obtained yields pure acetaldehyde on redistillation over fused $CaCl_2$.

Manufacture of acetaldehyde.

(*Synthetical process*)

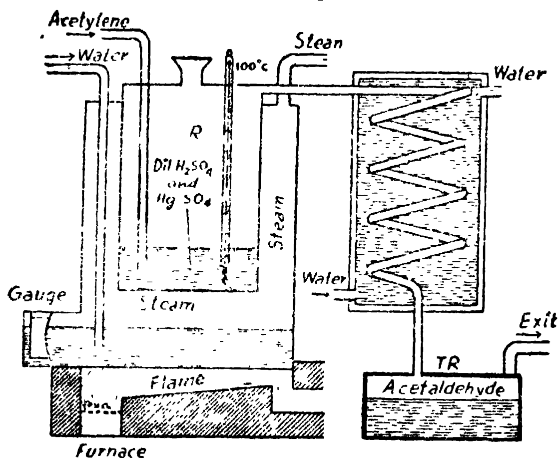


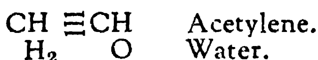
Fig. 27.

Acetaldehyde is manufactured synthetically these days from acetylene (CH≡CH) gas.

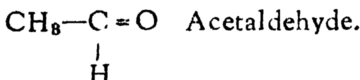
The apparatus for the synthesis of acetylene (CH≡CH) consists of a retort R provided with an inlet tube and also an out-let tube which is connected with a worm condenser, opening into a tank receiver TR. The retort R is jacketed with an outer vessel, provided with an arrangement to heat the retort R by steam.

A solution of murcuric sulphate in dilute H_2SO_4 is taken in the retort R and is saturated with acetylene gas (prepared by the action of water on calcium carbide) through the inlet tube as shown in fig. 27. As the solution gets saturated with the gas, the retort is heated to 100°C by steam, when acetaldehyde, passing through the worm condenser, condenses and collects in the tank receiver TR.

Reaction.



Acetylene.
Water.



Acetaldehyde.

Note :—The solution of mercuric sulphate in dilute H_2SO_4 acts as a catalyst in the hydrolysis of acetylene.

The acetaldehyde so synthesised gives acetic acid on commercial scale, when the acetaldehyde is oxidised with the atmospheric oxygen in the presence of manganese acetate or iron, which acts as a catalyst.

Properties of acetaldehyde.

Physical.

It is a colourless liquid, having a characteristic smell. It is soluble in water and also in organic solvents.

Chemical.

(Read table No: 10 and next table No: 11, followed by the examples of polymerisation and condensation from page 130 to 132).

Sensitive test for acetaldehyde.

Remine's Test. (Read page 135).

Uses of acetaldehyde.

It is used

(1) in the manufacture of resin, acetic acid, colouring matter and medicines,

(2) as a solvent for organic substances.

Laboratory method for the preparation ot acetone.

It consists in dry distillation of calcium acetate. About 20 grams of calcium acetate are strongly heated in a retort, connected with a condenser and a

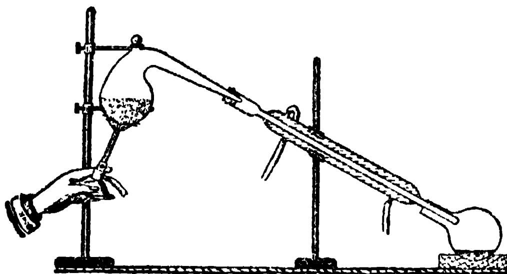
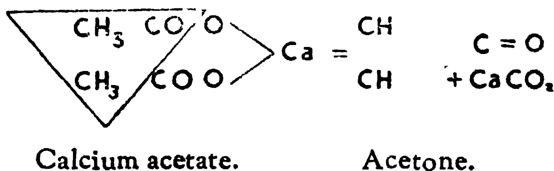


Fig. 28.

receiver as shown in fig. 28. An impure sample of acetone collects in the receiver.

Reaction.



Purification of acetone.

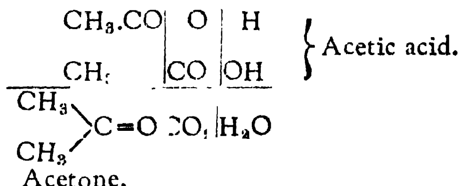
The impure sample of acetone is agitated with sodium hydrogen sulphite, which combines with acetone forming aceto-sodium hydrogen sulphite—a white and crystalline substance, which, when distilled with Na_2CO_3, yields pure acetone.

Manufacture of acetone.

1. Commercially, acetone is obtained as a *byproduct* in the manufacture of methyl alcohol.

2. It is also manufactured by passing the vapour of acetic acid over heated aluminium oxide (Al_2O_3), with acts as a catalyst.

Reaction.



It is manufactured by fermenting starch grains with the help of *bacillus-aceto-ethylicus* as ferments.

Properties of acetone.

Physical.

It is a colourless liquid possessing a pleasant smell. It boils at 56°C. It is very soluble in water and is a useful solvent of organic substances.

Chemical.

Read table No: 10, and also the table No: 11, followed by the examples of condensation on page 132.

Sensitive test of acetone.

Take a freshly prepared strong solution of sodium nitroprusside. Add just a drop of acetone to this solution and make it alkaline by adding caustic soda solution drop by drop. If it imparts a red colour to the solution the presence of acetone is confirmed.

Uses of acetone.

Acetone is used

1. in the manufacture of (1) chloroform, (2) iodoform and (3) cordite which is an explosive,

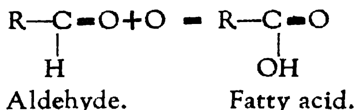
2. as a solvent for celluloid, nitrocellulose and other organic substances.

CHAPTER VII.

FATTY ACIDS.

We have seen on page 122, that fatty acids are the oxidation products of aldehydes.

Reaction.



General formula of fatty acid is $R-\underset{OH}{\underset{|}{C}}=O$

Hence, the carboxylic group of a fatty acid is $-\underset{HO}{\underset{|}{C}}=O$

Graphic formula of some of the members of fatty acids corresponding to their respective aldehydes are noted in the following table No: 12.

Table No: 12.

No. of carbon atoms.	Aldehydes		Fatty Acids	
	Names.	Constitutions.	Names.	Constitutions.
1.	Formaldehyde.	$H-C(=O)-H$	Formic acid.	$H-C(=O)-HO$
2.	Acetaldehyde.	$CH_3-C(=O)-H$	Acetic acid.	$CH_3-C(=O)-HO$
3.	Propaldehyde.	$C_2H_5-C(=O)-H$	Propionic acid.	$C_2H_5-C(=O)-HO$
...	....	....	....	....
...	....	....	....	....
...	....	....	....	....

16.	Palmaldehyde.	$C_{15}H_{81}—C(H)=O$	Palamatic acid.	$C_{15}H_{81}—C(HO)=O$
18.	Stearaldehyde.	$C_{17}H_{35}—C(H)=O$	Stearic acid.	$C_{17}H_{35}—C(HO)=O$

Note :—The first two members of the fatty acids, namely formic and acetic acids shall be studied in some detail. The last two are the higher fatty acids and we shall make a reference of them at a later stage in the study of *soaps*, which are sodium or potassium salts of higher fatty acids.

General methods for the preparation of fatty acids.

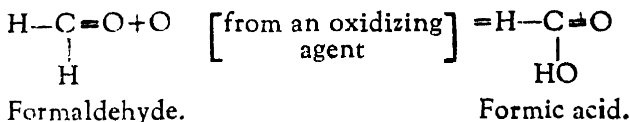
1. *The first general method.*

It consists in oxidising an aldehyde. (For the general reaction of this method refer to page 122).

Preparation of formic and acetic acids by the above method.

These acids are prepared by the oxidation of formaldehyde and acetaldehyde.

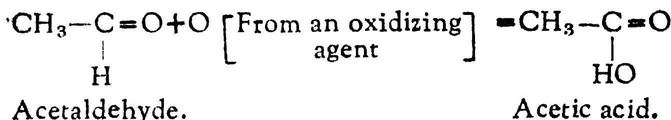
(*a*) *Reaction for formic acid.*



$$H-\underset{\substack{|\\ H}}{C}=O+O\ \left[\text{from an oxidizing agent}\right] = H-\underset{\substack{|\\ HO}}{C}=O$$

Formaldehyde. Formic acid.

(*b*) *Reaction for acetic acid.*



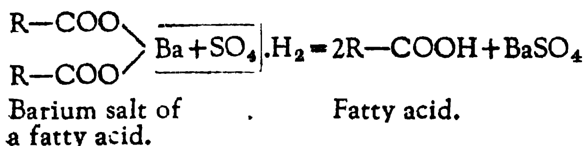
$$CH_3-\underset{\substack{|\\ H}}{C}=O+O\ \left[\text{From an oxidizing agent}\right] = CH_3-\underset{\substack{|\\ HO}}{C}=O$$

Acetaldehyde. Acetic acid.

2. *The second general method.*

It consists in treating sulphuric acid with the barium salt of the acid which is to be prepared.

General Reaction.

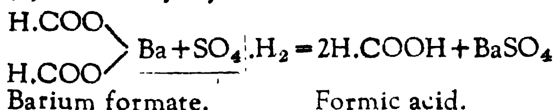


$$\begin{matrix} R-COO \\ R-COO \end{matrix}\!\!>\!\! \left.\overline{\underline{Ba+SO_4}}\right|.H_2 = 2R-COOH+BaSO_4$$

Barium salt of a fatty acid. . Fatty acid.

Preparation of formic and acetic acids by the above method.

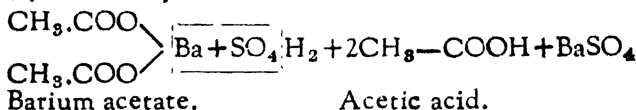
(*a*) *Rcaction for formic acid.*



$$\begin{matrix} H.COO \\ H.COO \end{matrix} \rangle Ba + SO_4 .H_2 = 2H.COOH + BaSO_4$$

Barium formate. Formic acid.

(*b*) *Reaction for acetic acid.*



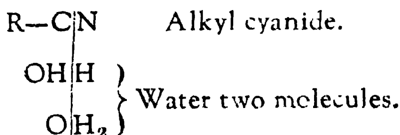
$$\begin{matrix} CH_3.COO \\ CH_3.COO \end{matrix} \rangle Ba + SO_4 H_2 + 2CH_3—COOH + BaSO_4$$

Barium acetate. Acetic acid.

3. *The third general method.*

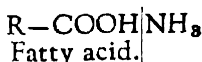
It consists in hydrolysing an alkyl cyanide.

General Reaction.



R—C N Alkyl cyanide.

OH H
O H$_2$ Water two molecules.

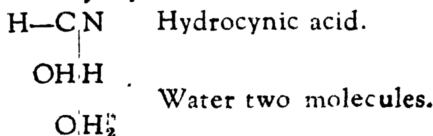


R—COOH NH$_3$

Fatty acid.

Preparation of formic and acetic acids by the above method.

(*a*) *Reaction for formic acid.*



H—C N Hydrocynic acid.

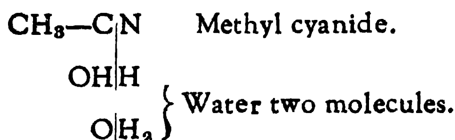
OH H
O H$_2$ Water two molecules.



H—COOH NH$_3$

Formic acid.

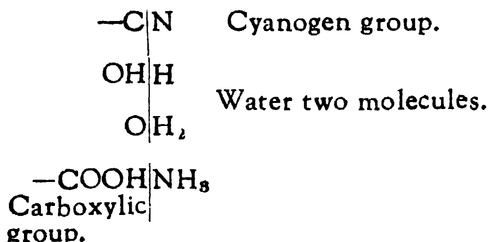
(*b*) *Rcaction for acetic acid.*



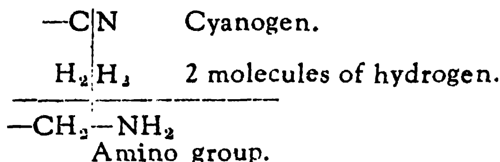


Nnte :—The cyanogen group (—CN), attached to a carbon atom in *any* organic compound, on hydrolysis is changed into a carboxylic group (COOH); whereas, on reduction it is changed into an amino group (—NH_2), according to the following general reactions :—

(*a*) *Hydrolysis of the cyanogen group.*



(*b*) *Reduction of the cyanogen group.*



General properties of fatty acids.

Physical.

The first three members of the fatty acids are colourless liquids, having a penetrating smell. The fourth and the a few next members are thick oily liquids possessing a disagreeable smell. The higher members are solid. They are all soluble in water and in organic solvents.

Chemical.

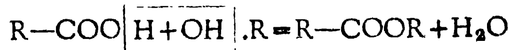
The general chemical reactions.

(Every general reaction will be illustrated by formic and acetic acids).

1. *The gneeral reactions of fatty acids on* ***alcohols.***

When fatty acids act on alcohols, the hydrogen atom of the carboxyl group combines with the hydroxyl group of the alcohol, forming water and a compound called *Ester.* The reaction is known as *Esterification*, which is always a reversible reaction. Read the page 71.

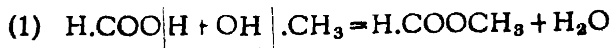
Reaction.



$$R{-}COO|H+OH|.R = R{-}COOR + H_2O$$

Fatty acid. Alcohol. Ester.

The above reaction is illustrated in the case of **formic** *and* **acetic acids** *acting on* **methyl** *and* **ethyl alcohols.**



(1) $$H.COO|H+OH|.CH_3 = H.COOCH_3 + H_2O$$

Formic acid Methyl alcohol. Methyl formate.



(2) $$H.COO|H+OH .C_2H_5 = H.COOC_2H_5 + H_2O$$

Ethyl alcohol. Ethyl formate.



(3) $CH_3.COO|H+OH|.CH_3 = CH_3.COOCH_3 + H_2O$

Acetic acid. Methyl alcohol. Methyl acetate.



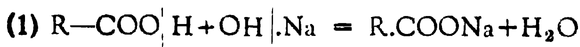
(4) $CH_3.COO|H+OH|.C_2H_5 = CH_3.COOC_2H_5 + H_2O$

Ethyl alcohol. Ethyl acetate.

2. *The general reactions of fatty acids on caustic soda or potash and ammonium hydroxide.*

When fatty acids act on any one of these alkali, the hydrogen atom of the carboxyl group combines with the hydroxyl group (—OH) of the alkali, forming water and a compound called a *salt*. The reaction is known as *neutralisation*.

Reactions.



(1) $R—COO|H+OH|.Na = R.COONa + H_2O$

Sodium salt of a fatty acid.

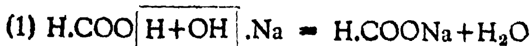


(2) $R—COO|H+OH|.NH_4 = R—COONa + H_2O$

Ammonium salt of a fatty acid.

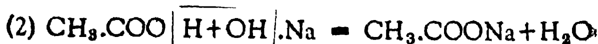
Note :—If, however, higher fatty acids like palmatic and stearic acids are neutralised by caustic soda or potash, we get water and a *soap*, which is a sodium or potassium salt of a higher fatty acid.

The above reactions are illustrated in the **formic** *and* **acetic acids** *acting on* **caustic soda** *or* **potash** *and* **ammonium hydroxide.**



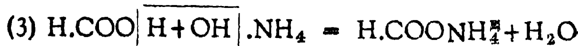
$$\text{(1) } H.COO\boxed{H+OH}.Na = H.COONa + H_2O$$

Formic acid. Sodium formate.



$$\text{(2) } CH_3.COO\boxed{H+OH}.Na = CH_3.COONa + H_2O$$

Acetic acid. Sodium acetate.



$$\text{(3) } H.COO\boxed{H+OH}.NH_4 = H.COONH_4 + H_2O$$

Formic acid. Ammonium formate.



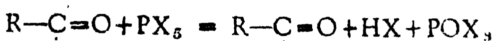
$$\text{(4) } CH_3.COO\boxed{H+OH}.NH_4 = CH_3COONH_4 + H_2O$$

Acetic acid. Ammonium acetate.

3. *The general reaction of fatty acids on phosphorus pentahalide.*

When fatty acids act on phosphorus pentahalide, the hydroxyl group (—OH) of the fatty acid $R-\underset{HO}{\underset{|}{C}}=O$ is replaced by one atom of the halogen, changing the acid into the corresponding *acid chloride* and forming also a halogen acid along with phosphorus oxyhalide.

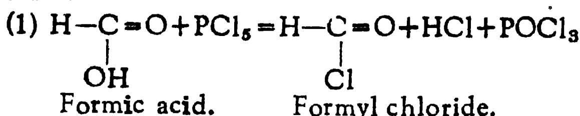
Reaction.



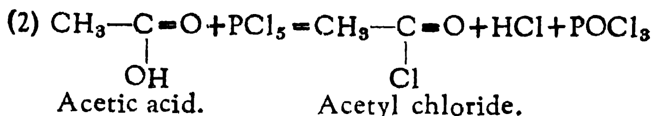
$$R-\underset{OH}{\underset{|}{C}}=O + PX_5 = R-\underset{X}{\underset{|}{C}}=O + HX + POX_3$$

Fatty acid. Acid halide.

The above reactions are illustrated in the case of **formic** *and* **acetic acids** *acting on* **phosphorus penta-chloride.**



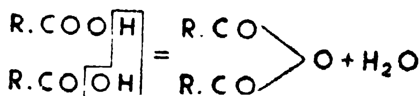
Note :—Formyl chloride is a very unstable compound and decomposes immediately forming HCl and CO.



4. *The general behaviour of fatty acids, when they are treated with a dehydrating agent.*

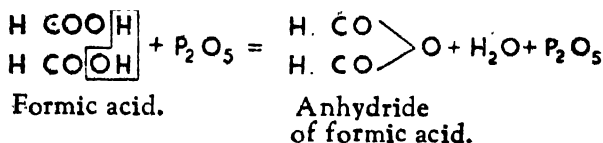
When fatty acids act on a suitable dehydrating agent like P_2O_5, they form *acid anhydride* and liberate water.

Reaction.



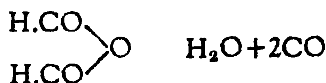
The molecules of a fatty acid. Acid anhydride.

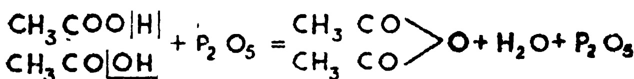
The above reactions are illustrated in the case of **formic** *and* **acetic acids** *acting on* **phosphorus penta-oxide.**



Formic acid. Anhydride of formic acid.

Note :—Anhydride of formic acid, being very unstable, soon decomposes into water and carbon-monoxide.





Acetic acid. Acetic anhydride.

FORMIC ACID

Laboratory method for the preparation of formic acid.

It consists in heating glycerine and oxalic acid in the proportion of 1 : 2 in a distilling flask fitted up with a condenser, a receiver and also a thermometer, having its bulb dipped in the liquid, as shown in the Fig. 29. The flask is heated over a sand bath and the temperature, during distillation is maintained between 105°C and 110°C. The distillate collects as an aqueous solution of formic acid. The reaction takes place in the following three stages :—

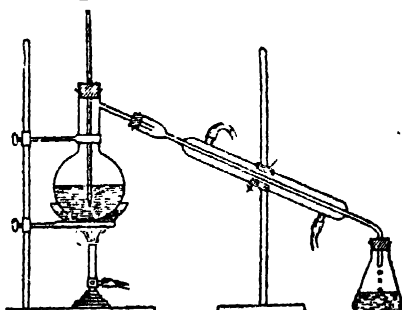
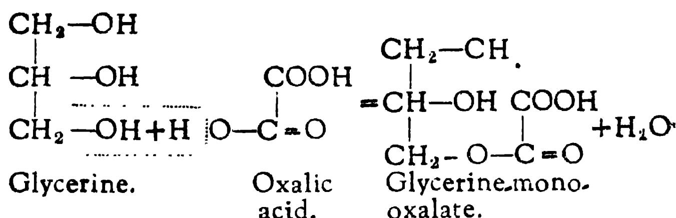
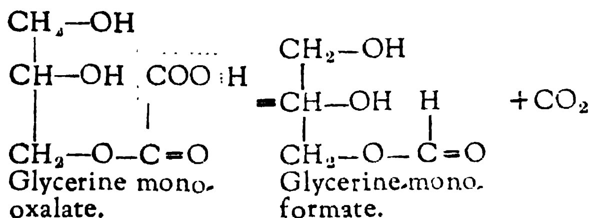


Fig. 29.

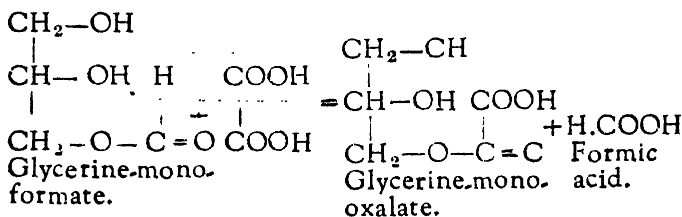
1. Esterification, resulting in the formation of glycerine-mono-oxalate and water.



2. The decomposition of glycerine-mono-oxalate into glycerine-mono-formate and carbon-dioxide.



3. The reaction of glycerine-mono-formate with more of oxalic acid forming (1) glycerine-mono-oxalate and (2) formic acid.



Notes :—1. Glycerine-mono-oxalate keeps up the chain of reactions with oxalic acid, as more of it is added a fresh.

2. Formic acid collects in an aqueous form, from which an anhydrous sample of it is obtained.

3. A small amount of glycerine will thus be needle to decompose large amount of oxalic acid into formic acid and carbon. dioxide.

Conversion of an aqueous formic acid into an anhydrous sample.

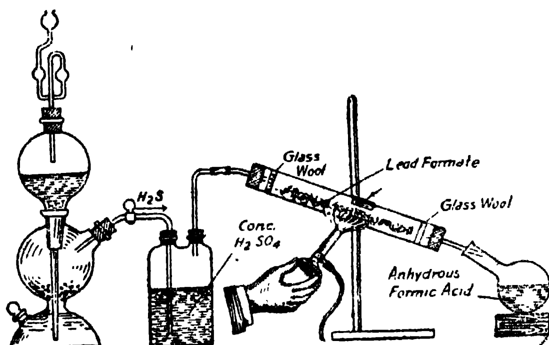
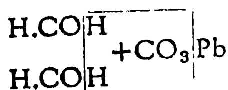
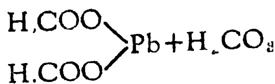


Fig. 30.

The aqueous formic acid is boiled with lead carbonate, the excess of which is removed by filtration. The filtrate is boiled to the point of saturation and then cooled. The lead formate is crystallised, separated out and completely dried.

Reaction.



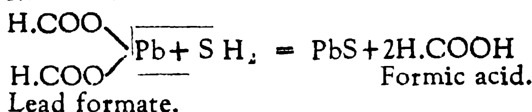


Formic acid. Lead formate.

The perfectly *dry* lead formate so obtained is loosely filled into a combustion tube clamped to a stand in an inclined position as shown in the Fig. 30. The upper end of this tube is connected to a H_2S gas generating Kipp's apparatus through a wash bottle

containing conc : H_2SO_4. As a current of *dry* H_2S gas is passed through the heated lead formate in the combustion tube, an anhydrous formic acid distills over and collects in the receiver.

Reaction.



$$\begin{matrix} H.COO \\ H.COO \end{matrix} \Big> Pb + S H_2 = PbS + 2H.COOH$$

Lead formate. Formic acid.

Manufacture of formic acid.

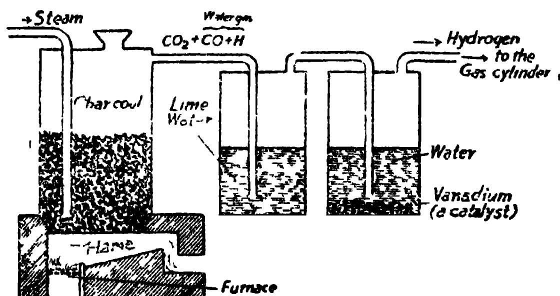


Fig. 31.

Steam under pressure is passed over heated charcoal in a retort as shown in the Fig. 31. A mixture of carbon-dioxide and water gas (carbon-monoxide and hydrogen) is led through a tank containing lime water, which absorbs CO_2 and is precipitated as $CaCO_3$. The water gas (CO and H) leaving the lime tank, passes through water in the presence of vanadium (a catalyst) in the next tank. The carbon-monoxide acts on water in the presence of the catalyst and forms formic acid. The hydrogen from this tank is led to the gas holder.

Reaction.



$$CO + H_2O = H.COOH$$

Formic acid.

Properties of formic acid.

Physical.

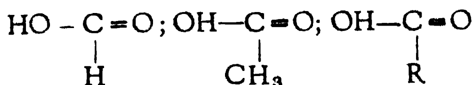
It is a colourless liquid, possessing a pungent, irritating and characteristic smell. It has a corrosive action on skin. It is heavier than water, in which it is highly soluble.

Chemical.

(Read pages 149 to 153).

The points, in which **formic acid** *differs from* **acetic** *or other* **fatty acids.**

(1) Formic acid alone contains in its constitution an aldehydic group shown below, as enclosed by dotted lines and hence, like other aldehydes, it behaves as a reducing agent. It is able to reduce ammonical solution of silver nitrate to metallic silver. Acetic acid and other higher members, have no aldehydic group and they are, therefore, not a reducing agent.



Formic acid. Acetic acid. Fatty acid.

(2) Formic acid is decomposed with conc : H_2SO_4 giving water and carbon-monoxide.

Reaction.



$$H{-}COOH + H_2SO_4 = H_2O + CO + H_2SO_4$$

Test of formic acid and formates.

(1) They evolve carbon-monoxide with strong H_2SO_4.

(2) Ferric chloride solution added to a neutral solution of formates ptoduces a red colour, which is discharged by dilute HCl.

ACETIC ACID.

Laboratory method for the preparation of acetic acid

A solution of 15 grams of powdered $K_2Cr_4O_7$ in 300 c.c. of water and 30 c.c. of strong H_2SO_4, is taken in a flask which is provided with a *reflex* condenser and is heated over a sand bath. About 20 c.c. of ethyl alcohol are introduced into the flask little by little, from the dropping funnel fitted to the reflex condenser, as shown in the Fig. 32. The mixture is heated *gently* for 30 minutes, till there is no smell of acetaldehyde in the flask.

Reaction.

(Read page 137).

The acetaldehyde produced during the reaction is reflexed back into the flask, and is oxidised to *acetic acid.*

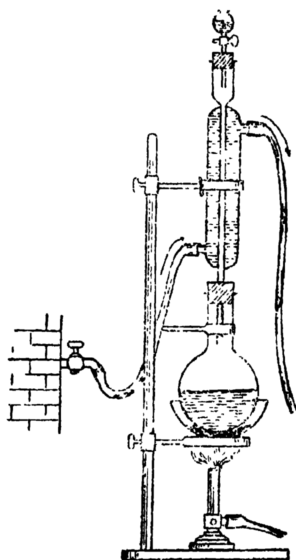
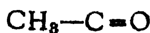


Fig. 32.

Reaction.






$$\underset{\text{Acetaldehyde.}}{CH_3-\underset{\displaystyle H}{\overset{|}{C}}=O} + O \qquad \underset{\text{Acetic acid.}}{CH_3-\underset{\displaystyle OH}{\overset{|}{C}}=O}$$

The contents of the flask are next transferred to a distilling flask fitted up as shown on page 13, fig. 4. Acetic acid is distilled out along with water, which collects in the receiver.

Conversion of aqueous acetic acid into anhydrous or glacial acetic acid.

The ditillate from the receiver is *just* neutralised with Na_2CO_3 and we get a solution of sodium acetate. This is boiled to the point of saturation, cooled and allowed to crystallise. The crystalls of sodium acetate ($CH_3.COONa.3H_2O$) are separated out, dried and finally fused to remove the water of crystallisation. The anhydrous sodium acetate ($CH_3.COONa$) is next distilled with conc : H_2SO_4. The distillate on cooling solidifies as an *anhydrous* or *glacial acetic acid.*

Notes :—(1) Glacial acetic acid is a white *icy* crystalline solid.

(2) Acetic acid does not solidify unless free from impurities like water even in traces.

Manufacture of acetic acid.

1. Vinegar process.

Acetic acid is manufactured in a "Vat", having a perforated shelf at the bottom and also at the top as shown in the Fig. 33. The space between these two shelves is packed up with wood shavings soaked in strong "*Vinegar*"—a solution of acetic acid having also a living *fungus* (*bacteria*) called *mycoderma aceti* – a *ferment.* The "Vat" is provided with appertures for the supply of atmospheric oxygen from outside. About 5% of ethyl alcohol, is run down slowly from the top into the "Vat".

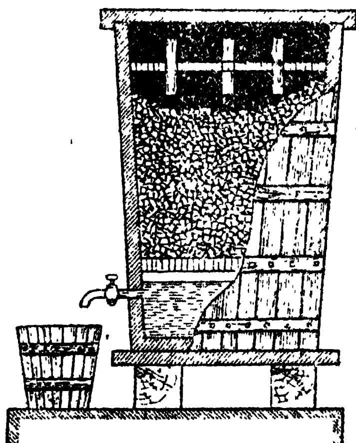


Fig. 33.

The alcohol, during its passage through the wood shavings is oxidised to acetic acid by an **Enzyme**—a complex organic catalyst produced from the *ferment* **Mycoderma Aceti.**

Reaction.



$$CH_3.CH_2.OH+2O = CH_3.COOH+H_2O$$

Ethyl alcohol. Acetic acid.

The acetic acid is drained out from the bottom of the "Vat". The concentration of the acetic acid is increased by passing the liquid through the wood shavings from the top of the "Vat" over and over again.

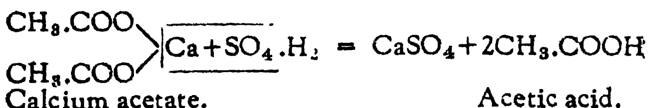
2. Synthetic process.

It is commercially obtained synthetically from acetylene. (Refer to pages 138 and 139, Fig. No. 27).

3. From pyroligneous acid.

The calcium acetate, obtained during the distillation of pyroligneous acid. (Read page 86, and also Fig. No: 20, on page 86), is the source from which acetic acid is obtained on a commercial scale. The calcium acetate is distilled with sulphuric acid.

Reaction.



$$\begin{matrix} CH_3.COO \\ CH_3.COO \end{matrix}\Big\rangle \overline{Ca+SO_4}.H_2 = CaSO_4+2CH_3.COOH$$

Calcium acetate. Acetic acid.

Note :—In all these commercial processes, only an aqueous solution of acetic acid is obtained. For the conversion of aqueous acetic acid into glacial acetic acid, read page 159.

Properties of acetic acid.

Physical.

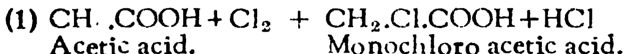
At ordinary temperature it is a colourless liquid; but at a low range of temperature, it is a white crystalline *icy* solid. It is highly soluble in water and possesses a very characteristic smell. It absorbs moisture from air. It boils at 118°C. It is denser than water. In concentrated form, it burns skin, producing blisters.

Chemical.

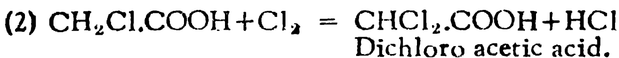
(Read pages 149 to 158).

Apart from the properties of the acetic acid already described, it is important to know that acetic acid also yields mono, di or tri substitutive products, when the acetic acid is treated with chlorine or bromine in sunlight.

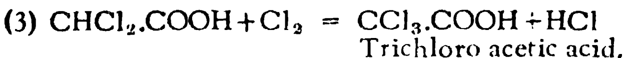
Reactions.



(1) $CH\ .COOH + Cl_2 + CH_2.Cl.COOH + HCl$
Acetic acid. — Monochloro acetic acid.



(2) $CH_2Cl.COOH + Cl_2 = CHCl_2.COOH + HCl$
Dichloro acetic acid.



(3) $CHCl_2.COOH + Cl_2 = CCl_3.COOH + HCl$
Trichloro acetic acid.

Uses of acetic acid

It is used :—

(1) in obtaining rubber form latex,

(2) in obtaining casein from milk,

(3) in the manufacture of dyes, drugs, perfumes and artificial silk,

(4) in varnishing "canvas" in combination with cellulose.

(5) in the production of cinematographic films,

(6) in the manufacture of various acetates of commercial importance,

(7) as a solvent of organic substances.

Test of acetic acid and acetates.

(1) Acetates, when just warmed with a few drops of conc : H_2SO_4 give characteristic smell of acetic acid.

(2) A neutral solution of an acetate gives a red colour with ferric chloride. The red solution, however, gives a brown precipitate of iron basic acetate on boiling the solution.

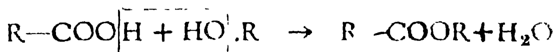
CHAPTER VIII.

ESTERS AND SALTS.

(A) Esters

Esters are the compounds formed by the action of alcohols on fatty or mineral acids. The reaction is known as *Esterification,* which is a reversible type of reaction, since every ester is easily hydrolysed. (Read pages 71 to 72).

General Reactions.



$$R{-}COO|H + HO|.R \rightarrow R{-}COOR + H_2O$$

Fatty acid. Alcohol. Ester.



$$XH + OH.R \rightarrow RX + H_2O$$

Mineral Alcohol. Ester.

Note :—In the preparation of an ester, the experiment has to be so modified as to prevent the back reaction. This is usually done by using a *condensing reagent*, like conc : H_2SO_4 or fused $ZnCl_2$, which is an absorbent of water Hence, water formed during the esterification is absorbed by the condensing reagents and the hydrolysis of ester is prevented.

We shall study a few important esters :—

1. Ethyl acetate.

Preparation of ethyl acetate.

We take a mixture of ethyl alcohol and conc : H_2SO_4 in equal volumes, into a distilling flask DF, fitted with a dropping funnel, a condenser and a receiver as shown in the Fig. 34. The flask is heated over a sand bath. As the temperature of the mixture rises to 140°C, a mixture of ethyl alcohol and glacial acetic acid taken in the dropping funnel in equal volumes, is run down into the flask DF, at the same, rate, at which *ethyl acetate* distills over and collects into the receiver. The esters so prepared is impure, as it contains, ethyl alcohol, acetic acid, sulphurous acid and water.

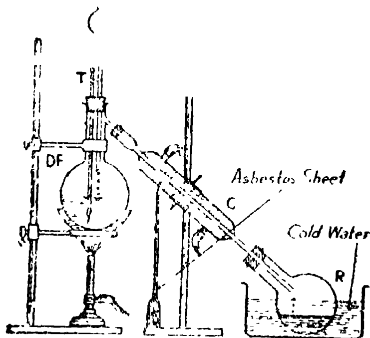
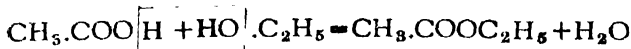


Fig. 34.

Reaction.



$$CH_3.COO\boxed{H + HO}.C_2H_5 = CH_3.COOC_2H_5 + H_2O$$

Acetic acid. Ethyl acetate.

Note :—Conc : H_2SO_4 has been used as a *condensing reagent* to prevent the back reaction.

Purification of ethyl acetate.

The impure ethyl acetate is throughly shaken in a separating funnel with a strong solution of

Na_2CO_3. The acids present therein are thus neutralised. On allowing the mixture to stand, the aqueous salt solution, being havier than alcoholic ethyl acetate, forms the lower layer in the separating funnel as shown in the Fig. 35. After the aqueous solution is allowed to drain out the alcoholic ethyl acetate, is next treated with a strong NaCl solution, which dissolves the alcohol, and which being havier forms the lower layer on standing. The liquid forming the lower layer is drained out, leaving ethyl acetate with water in traces. The ester is finally dehydrated with fused $CaCl_2$ for over a night

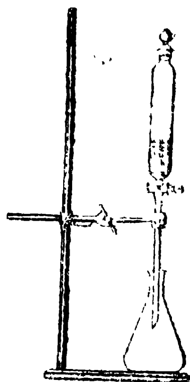


Fig. 35.

Properties of ethyl acetate.

Physical.

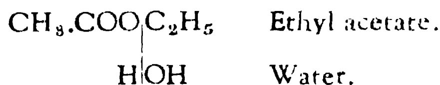
It is a colourless liquid, possessing a sweet fruity smell. It is in soluble in water but soluble in alcohol and ether. It is lighter than water.

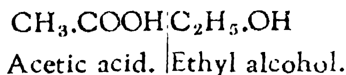
Chemical.

1. *Action of water on ethyl acetate.*

It is hydrolised with water, giving acetic acid and alcohol.

Reaction.

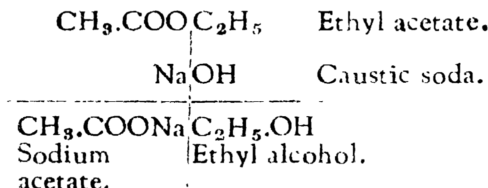




2. *Action of caustic soda or potash on the ester.*

It is decomposed with NaOH or KOH, giving sodium or potassium acetate and ethyl alcohol.

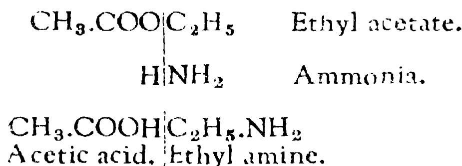
Reaction.



3. *Action of ammonia on the ester.*

It acts on ammonia, giving acetic acid and ethyl alcohol.

Reaction.



Hydrolysis of ethyl acetate.

Ethyl acetate when hydrolised gives acetic acid and ethyl alcohol. For hydrolising ethyl acetate, we take 30 c.c. of ethyl acetate and 60 c.c. of caustic potash solution of nearly 15N strength in a flask fitted up with a reflex condenser as shown in Fig. 32. (Refer to page 158). Heat the flask over a water bath, until the upper layer of the ester disappears, indicating that the ethyl acetate is completely hydrolised into alcohol and sodium acetate. Next, the liquid is transfered into a simple distilling arrangement and the alcohol is distilled. The sodium acetate is left in the distilling flask. The acetic acid can now easily be obtained from the sodium acetate, when it is distilled with H_2SO_4.

Esters are prepared on the principle adopted in the procedure for the preparation of ethyl acetate. Esters mostly are good solvent for organic sub-stances. Some of them are the odorous principle of various plants. They are, therefore, used as *perfumes* and as flavouring *essences*. As for example :—

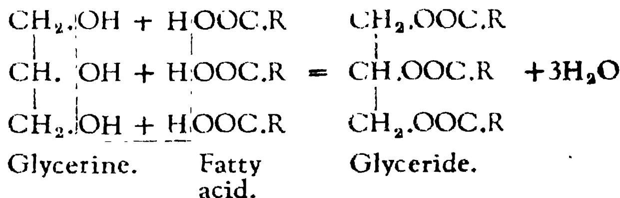
1. *Amyl acetate.*
2. *Amyl butyrate.*
3. *Ethyl butyrate.*

They are used as organic solvents and artificial fruit essences in *sweets* and *cold drinks*.

4. *Glycerides.*

They are the esters of higher fatty acids (palmatic and stearic acids) with glycerine or glycerol which is the trihydroxy alcohol of propane. The vegetable oils, fats, waxes and butter are glycerides. They are the source, from which ***soap*** and ***glycerine*** or ***glycerol*** are commercially obtained.

General reaction involved in the formation of glycerides.



$$\begin{array}{l} CH_2.OH + H.OOC.R \\ CH.OH + H.OOC.R \\ CH_2.OH + H.OOC.R \end{array} = \begin{array}{l} CH_2.OOC.R \\ CH.OOC.R \\ CH_2.OOC.R \end{array} + 3H_2O$$

Glycerine. Fatty acid. Glyceride.

Notes :—(1) The glycerides are named by using "**in**" as a suffix to the name of fatty acids entering into the composition of glycerides.

(2) The three "acid radicals" acting on the glycerol may be ***identical*** or ***different***.

Some of the higher fatty acids and their corresponding glycerides with their names and constitutions in the following table No: 13 :—

Table No: 13.

	Fatty acids.		Glycerides.	
	I Names.	II Constitutions.	III Names.	IV Constitutions.
Saturated acids.	1. Palmatic acid.	$C_{15}H_{31}.COOH$	Palmatin.	$CH_2.OOC.C_{15}H_{31}$ $CH.OOC.C_{15}H_{31}$ $CH_2.OOC.C_{15}H_{31}$
	2. Stearic acid.	$C_{17}H_{35}.COOH$	Stearin.	$CH_2.OOC.C_{17}H_{35}$ $CH.OOC.C_{17}H_{35}$ $CH_2.OOC.C_{17}H_{35}$
	3. Lauric acid.	$C_{11}H_{23}.COOH$	Laurin.	$CH_2.OOC.C_{11}H_{23}$ $CH.OOC.C_{11}H_{23}$ $CH_2.OOC.C_{11}H_{23}$

Unsaturated acids.	4. Lin olieic acid.	$C_{17}H_{31}.COOH$	Linolein.	$CH_2.OOC.C_{17}H_{31}$ $CH.OOC.C_{17}H_{31}$ $CH_2.OOC.C_{17}H_{31}$
	5. Erucic acid.	$C_{21}H_{41}.COOH$	Erucin.	$CH_2.OOC.C_{21}H_{41}$ $CH.OOC.C_{21}H_{41}$ $CH_2.OOC.C_{21}H_{41}$
	6. Oleic acid.	$C_{17}H_{33}.COOH$	Olein.	$CH_2.OOC.C_{17}H_{33}$ $CH.OOC.C_{17}H_{33}$ $CH_2.OOC.C_{17}H_{33}$

Examples of glycerides are :—

Fats, vegetable oils, butter and waxes.

Fats are the glycerides of *saturated* higher fatty acids. Palmatin and stearin are the examples of fats. They are all solid at ordinary temperature and pressure. (Read column III, table No: 13, page 168).

Vegetable oils are the glycerides of ***unsaturated*** higher fatty acids. Olive oil (olein), linseed oil (linolein), and fish oil (erucin fish oil) are the examples of vegetable oils. They are all liquid at ordinary temperature. (Read column III, table No: 13, page 169).

Note :—Mineral oils are complex mixture of hydrocarbons in varying proportions. Petroleum, *kerosene oil, petrol, benzin* are the examples of mineral oils. (Read page 58).

Butter is a mixture of palmatin, stearin and butarin (glycerides of butyric acid) and a small quantity of water.

Waxes are esters (*not glycerides*) of higher alcohols. Myricyl alcohol —$C_{30}H_{61}.OH$ or cetyl alcohol —$C_{16}H_{33}$) with palmatic acid.

Note :—Vegetable oils, being liquid glycerides of unsaturated fatty acids are changed into artificial solid fats (margarine), when treated with hydrogen gas under pressure at 200°C in the presence of finely divided nickel, which acts as a *catalyst*. The process is commonly known as ***hydrogenation*** or ***hardening*** **of oils.**

2. Ethyl bromide.

It is an ester of ethyl alcohol with hydrobromic acid, which is a mineral acid.

Preparation of ethyl bromide.

Introduce 5 grams of phosphorus and 40 c. c. of ethyl alcohol into a distilling flask DF fitted up with a dropping funnel, which contains about 10 c, c. of bromine. Allow the bromine to run down *drop* by *drop* into the distilling flask kept submerged in ice cold water in a basin. After the entire amount of the bromine, is thus carefully introduced, the flask is left over night, during which period the following reactions are completed :—

Reactions.



(1) $P + 5Br = PBr_5$



(2) $C_2H_5.OH + PBr_5$ $\quad$ $C_2H_5.Br + HBr + POBr_3$
Ethyl bromide.

The ethyl bromide so prepared is next distilled over a water bath as shown in Fig. No: 36. The distillate is an impure sample of ethyl bromide. It is purified like ethyl acetate. (Read on page 164).

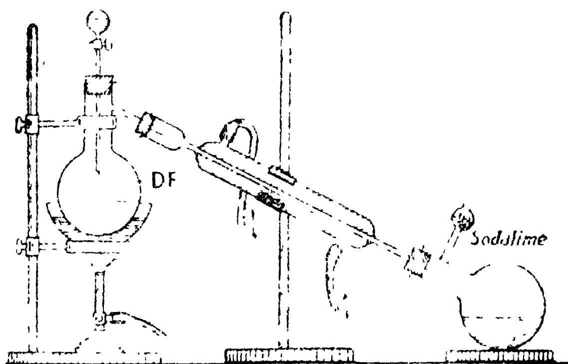


Fig. 36.

It is, however, to be noted that ethyl bromide, being heavier than water, will always form the lower layer in the separating funnel during its process of purification.

Properties of ethyl bromide.

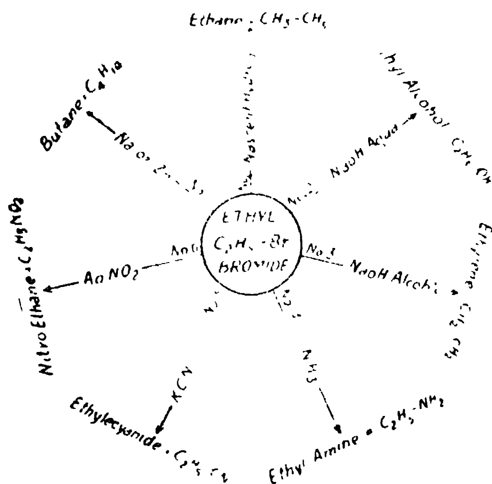
Physical.

It is a colourless liquid, possessing a smell like that of chloroform. It is in soluble in water, but soluble in organic solvents. It is heavier than water.

Chemical.

Its chemical properties can be studied by making a reference to the *seven general reactions of alkyl halides* from pages 62 to 64.

The seven reactions of ethyl bromide are sumerised diagrametrically.



3. Chloroform and iodoform.

Notes :—(1) They may be considered as tri-chloro and tri-iodo derivative of methane. They are, however, not usually prepared from methane.

(2) They cannot be prepared by esterification, because the tri-hydroxy alcohol of methane, being unstable is not known. Hence, chloroform and iodoform are not included amongst esters. Nevertheless, they may be treated as esters, since like esters they are hydrolised by caustic soda or potash. Refer to the property No: 3 of chloroform and iodoform in the table No: 14.

(a) Chloroform.

Preparation of chloroform.

Take a paste of 100 grams of bleaching powder $\left[Ca\begin{matrix} \diagup Cl \\ \diagdown OCl \end{matrix}\right]$ with 400 c.c. of water and 25 c.c. of ethyl alcohol, into a litre retort fitted up with a condenser and a receiver as shown in the Fig. 37. The paste

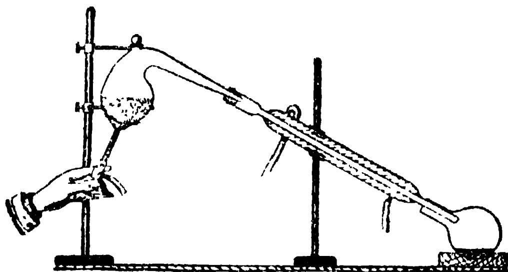
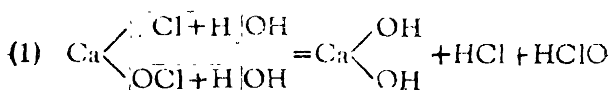


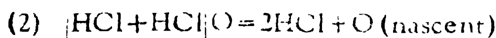
Fig. 37.

is first heated gently, till all the apparent reactions subside. Next, the temperature is gradually raised and distillation is continued, until heavy drops of chloroform cease to collect in the receiver.

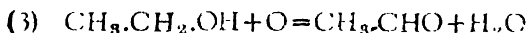
Reactions.



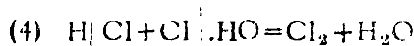
$$(1)\quad Ca\begin{cases}Cl + H\,|OH\\ OCl + H\,|OH\end{cases} = Ca\begin{cases}OH\\ OH\end{cases} + HCl + HClO$$



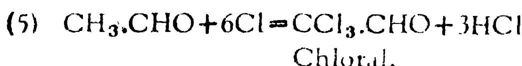
$$(2)\quad HCl + HCl|O = 2HCl + O \text{ (nascent)}$$



$$(3)\quad CH_3.CH_2.OH + O = CH_3.CHO + H_2O$$

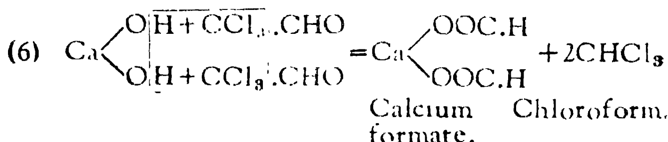


$$(4)\quad H|Cl + Cl|.HO = Cl_2 + H_2O$$



$$(5)\quad CH_3.CHO + 6Cl = CCl_3.CHO + 3HCl$$

Chloral.



$$(6)\quad Ca\begin{cases}O|H + CCl_3.CHO\\ O|H + CCl_3.CHO\end{cases} = Ca\begin{cases}OOC.H\\ OOC.H\end{cases} + 2CHCl_3$$

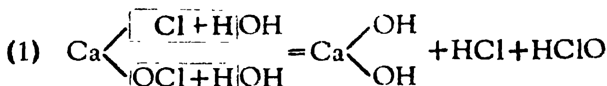
Calcium formate. Chloroform.

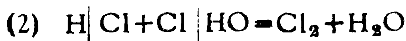
The chloroform so distilled is impure, the impurities being ethyl alcohol, hydrochloric acid and water. It is purified like ethyl bromide. (Read purification of ethyl bromide.

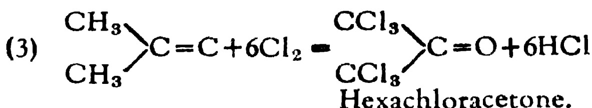
Manufacture of chloroform.

It is manufactured practically in the same way, as it is prepared in the laboratory. Only it is economical to use acetone instead of ethyl alcohol.

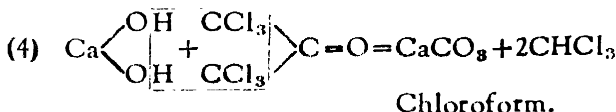
Reactions of acetone with bleaching powder paste.







Hexachloracetone.



Chloroform.

Properties.

Physical.

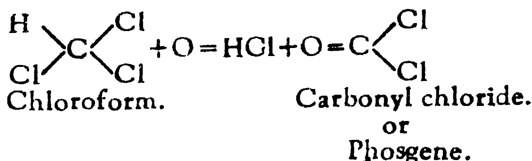
It is a colourless liquid, heavier than water, possessing a pleasant smell and sweet taste. It is insoluble in water, but soluble in organic solvents. It is a solvent for iodine.

Chemical.

1. It burns with a greenish flame at a high temperature.

2. It is readily oxidised by atmospheric oxygen, even if exposed to light.

Reaction.

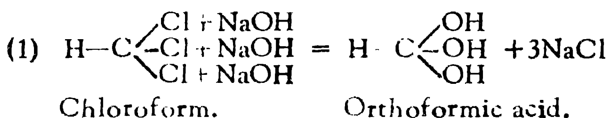


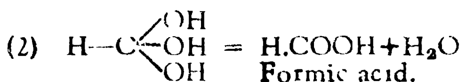
Chloroform. Carbonyl chloride. or Phosgene.

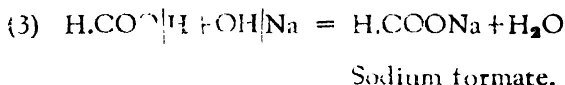
Note :—The carbonyl chloride or phosgene so produced is fatally poisonous. A sample of chloroform exposed to air or oxygen should not, therefore, be administered to a patient for surgical operation.

3. It is decomposed by caustic soda or potash, forming sodium chloride and orthoformic acid, the latter of which decomposes, yielding formic acid. This acid reacts on the excess of NaOH or KOH forming sodium or potassium formate.

Reactions.







4. Its vapour, if inhaled, produces unconsciousness on account of which, it is used as an anaesthetic in surgical operations.

Notes :—(1) Chloroform for surgical purposes is sold in blue or brown glass bulbs, drawn out to a sealed jet, to minimise the chances for oxidation.

(2) A sample of chloroform, exposed to the action of atmospheric oxygen, contains phosgene and hydrochloric acid, the

latter of which, being a strong electro. lyte,* ionises, introducing chlorine ions (Cl^-) which combine with silver ions (Ag^+) from silver nitrate solution forming silver chloride, which is soluble in dilute ammonia. A pure sample of chloroform, being a non.electrolyte,* fails to give a precipitate of AgCl with $AgNO_3$ solution.

**For electrolytes and non-electrolytes read appendix on electrovalency.*

Iodoform.

Preparation of iodoform.

Take 4 grams of crystalline Na_2CO_3 dissolved in 20 c. c. of water along with 2 c. c. of ethyl alcohol in a beaker, in which a thermometer is suspended. The solution in the beaker is heated over a water bath, as shown in Fig. No: 38. Two grams of iodine are next gradually added to the solution, with constant stirring. The solution is heated at a constant temperature of 70°C, till the solution becomes colourless and yellow crystalls of iodoform appear giving out its characteristic smell.

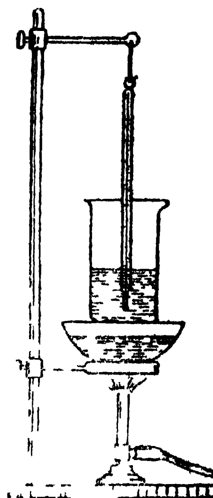


Fig. 38.

Reaction. [Read page 98].

Notes :—(1) *Acetone* also like *ethyl alcohol* yields iodoform crystalls with iodine and sodium carbonate solution.

(2) *Acetone* unlike ethyl alcohol yields iodo. form crystalls with iodine even in the presence of ammonia. [Read page 99].

Manufacture of Iodoform.

It is manufactured by the electrolysis of an alcoholic potassium iodide solution in an electrolytic cell, as shown in Fig. No: 39. The alcoholic solution of KI is introduced through the inlet tube T_1, into the electrolytic cell. As the current is switched on metallic potassium is liberated at the cathode, where it decomposes water and forms KOH and hydrogen gas. The iodine is liberated at the anode, where it acts on water forming a mixture of HI and HIO, the latter of which liberates oxygen, which oxidises the alcohol to acetaldehyde. As the stirrer S is made to churn the liquid in the cell, the acetaldehyde so obtained is changed ultimately into iodoform, the crystals of which are drained out through the outlet tube T_2. For reactions, read page 98.

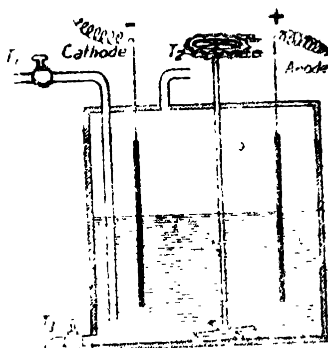


Fig. 39.

Properties.

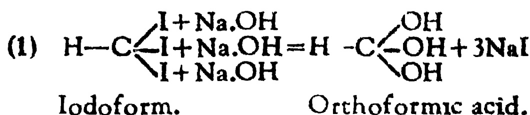
Physical.

It is a crystalline solid, possessing yellow colour, a disagreeable and characteristic smell. It is insoluble in water, but soluble in alcohol.

Chemical.

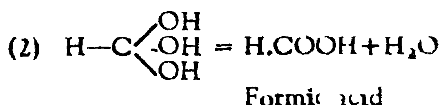
It is inflamable, like chloroform, it is also decomposed by caustic soda or potash forming sodium iodide and orthoformic acid, the latter of which is decomposed forming water and formic acid. The formic acid is neutralised by the caustic and forms sodium formate.

Reactions.



$$H-C\begin{cases}I+Na.OH\\I+Na.OH\\I+Na.OH\end{cases}=H-C\begin{cases}OH\\OH\\OH\end{cases}+3NaI$$

Iodoform. Orthoformic acid.



$$H-C\begin{cases}OH\\OH\\OH\end{cases}=H.COOH+H_2O$$

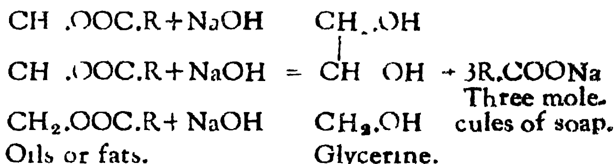
Formic acid

(4) It is poisonous and germicidal. Hence, it is used as an antiseptic to cover up wounds

(B) Salt

A soap is a sodium or potassium salt of higher fatty acids. It is obtained by the decomposition of fats and oils (glycerides of higher fatty acids) with an alkali solution, which is commercially known as ' lye".

General Reaction



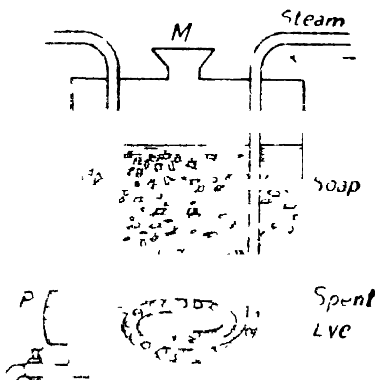
$$\begin{matrix}CH_2.OOC.R+NaOH & & CH_2.OH & \\ CH.OOC.R+NaOH & = & CH.OH & +3R.COONa \\ CH_2.OOC.R+NaOH & & CH_2.OH & \end{matrix}$$

Oils or fats. Glycerine. Three molecules of soap.

The process of decomposition of glycerides of higher fatty acids—oils and fats—with an alkali solution resulting in the formation of glycerine [a trihydroxy alcohol of propane [CH_2.OH. CH.OH. CH_2.OH] and soap, is known as ***saponification.***

Manufacture of soap

A melt of fats and oils is run down the inlet tube into a saponifying tank along with 10% "lye" which is nearly double the amount of the melt. Steam is passed through a copper worm into the mixture for about 6 to 8 hours for saponifying the fats and oils into *soap* and *glycerine*, both of which are soluble A solution of sodium chloride is next added through the inlet tube. *Soap* being insoluble in salt water, is precipitated and floats on the surface of the "*spent lye*". The process of precipitating soap with common salt solution is known as *salting out* of the soap. The "spent lye" containing *glycerine* is drained out through the outlet tube T, as shown in Fig 40. The soap thus left in the tank is once more treated with fresh "lye" for effecting *complete* saponification. The soap is reprecipitated by salting out.



Saponifying tank.
Fig. 40.

The "*spent lye*" collected after successive saponification is used as a source for the manufacture of glycerine described later

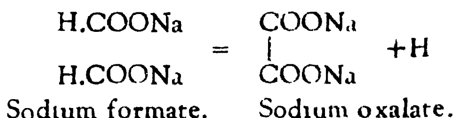
Soap, obtained after final salting out is next washed carefully to remove the excess of alkali and salt. Soap free from alkali is hardened, coloured, perfumed, cut to the size and stamped into tablets.

Hard and ***soft soap*** are manfactured by saponifying the fats and oils with caustic soda and potash

respectively. *Castile soap* is a hard soap manufactured from olive oil. *Transparent soap* is ordinary rosin soap, from which solid suspended impurities are removed by dissolving out rosin soap in alcohol. The clear alcoholic soap solution is run into bar moulds. As the alcohol is distilled off, solid bars of *transparent soap* are obtained. These bars are cut to proper size and stamped into tablets.

Importance of some of the salts of lower fatty acids.

1. *Sodium formate* :—On distillation, it gives sodium oxalate and hydrogen.



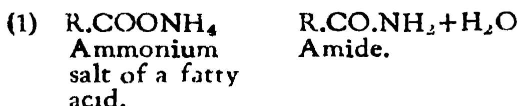
2. *Sodium acetate* – On distillation with caustic soda or potash, it gives, methane. [Read page 47]. This reaction is helpful in *going down the series*, discussed later.

3. *Calcium formate*.—On distillation, it yields formaldehyde. [Read page 104].

4. *Calcium acetate* :—On distillation, it yields acetone. [Read page 105]. A mixture of calcium salt of a fatty acid and calcium formate on distillation, gives an aldehyde, other than formaldehyde [Read page 104].

5. *Potassium cyanide* :—On treatment with an alkyl halide, it yields, an alkyl cyanide. [Read page 63]. This reaction is helpful in *going up the series* discussed later.

6. *Ammonium salt of a fatty acid.* :—On strongly heating or dehydrating it, we get an *amide* at first and ultimately an *alkyl cyanide.*



(1) $R.COONH_4$ → $R.CO.NH_2 + H_2O$
Ammonium salt of a fatty acid. — Amide.



(2) $R-CO.NH_2$ → $R-CN + H_2O$
Amide. — Alkyl cyanide.

Salts and Esters compared in a tabular form

Table No: 14.

Salts.	Esters.
1. They are the products of neutralization of an acid with a base.	1. They are the products of esterification of an acid with an alcohol.
2. They are solid	2 They are mostly liquid.
3. They are colourless and odourless	3. They generally possess a sweet and fruity smell and are used as fruit essences.
4. They are mostly soluble in water	4 They are insoluble in water, but soluble in organic solvents.
5. They are strong electrolytes and freely ionise.	5. They are non-electrolytes and do not ionise.
6. Only the salts formed by weak acids and weak bases are hydrolised.	6. They are all hydrolised.

CHAPTER IX.

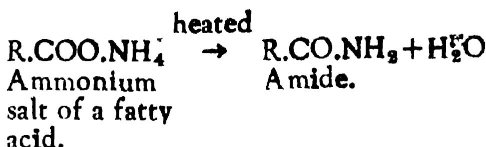
[This chapter is devoted to the study of ***amides, cyanides, amines, acid chlorides, acid anhydrides*** and ***ether***. Only ***typical members*** of these families will be considered].

Amides.

General formula :—**R.CO.NH$_2$.**

Group radical :—**[—CO—NH$_2$].**

General reaction for the preparation of amides.



$$R.COO.NH_4 \xrightarrow{\text{heated}} R.CO.NH_2 + H_2O$$

Ammonium salt of a fatty acid. → Amide.

Typical amide.

Acetamide :—CH$_3$ CO—NH$_2$.

It may be prepared by any of the two following methods :—

Preparation.

(1) A mixture of 25 grams of ammonium acetate and the same weight of glacial acetic acid is heated in the flask F, as shown in Fig. 41, till a few drops of free water and acetic acid begin to distill over. The distillation is continued for about 2 hours and the distillate collected in B is water and some acetic acid. The ammonium acetate decomposes.

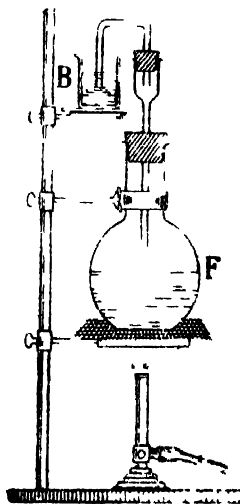


Fig. 41.

Reaction.




$CH_3.COONH_4$ $\quad$ $CH_3.CO.NH_2 + H_2O$

Ammonium acetate. $\quad$ Acetamide.

The residue, which is left in in the flask consists of acetamide and acetic acid, the mixture is next transferred into a distilling flask (fitted up with a

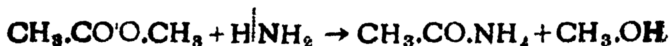


Fig. 42.

thermometer and *a long air condenser*) Fig. 42 and distilled. The distillate collecting at obout 230°C solidifies as acetamide in the receiver.

(2) Methyl acetate is dissolved in the same volume of strong ammonium hydroxide. The reaction between methyl acetate and strong ammonia is very slow. Hence, the mixture is allowed to stand for a couple of days and then it is fractionally distilled.

Reaction.



$$CH_3.CO'O.CH_3 + H|NH_2 \rightarrow CH_3.CO.NH_2 + CH_3.OH$$

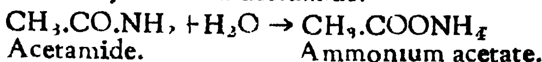
Properties.

Physical.

It is a colourless crystalline solid, smelling like mice. It is soluble in water and also in organic solvents.

Chemical.

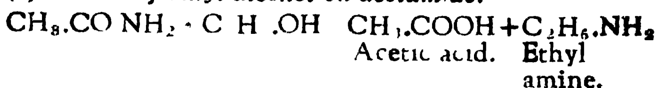
(1) *Action of water on acetamide.*



$$CH_3.CO.NH_2 + H_2O \rightarrow CH_3.COONH_4$$

Acetamide. Ammonium acetate.

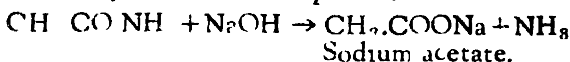
(2) *Action of ethyl alcohol on acetamide.*



$$CH_3.CO.NH_2 + C_2H_5.OH \quad CH_3.COOH + C_2H_5.NH_2$$

Acetic acid. Ethyl amine.

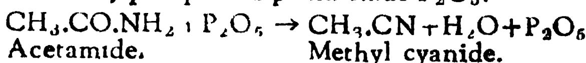
(3) *Action of caustic soda or potash.*



$$CH_3.CO.NH_2 + NaOH \rightarrow CH_3.COONa + NH_3$$

Sodium acetate.

(4) *Action of phosphorus penta-oxide P_2O_5.*

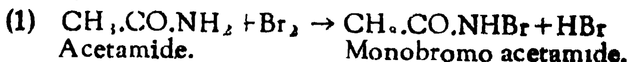


$$CH_3.CO.NH_2 + P_2O_5 \rightarrow CH_3.CN + H_2O + P_2O_5$$

Acetamide. Methyl cyanide.

(5) *Hofmann's Reaction.*

It is the treatment of bromine and caustic soda or potash on acetamide. The reaction proceeds in three stages :–

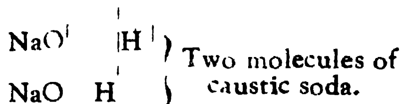


(1) $CH_3.CO.NH_2 + Br_2 \rightarrow CH_3.CO.NHBr + HBr$

Acetamide. Monobromo acetamide.



(2) $CH_3.CO.NH|Br$ Monobromo acetamide.



NaO | H } Two molecules of

NaO H } caustic soda.

↓



$CH_3.NH_2 + Na_2CO_3 + HBr.$

Methyl amine.



(3) $2HBr + 2NaOH \rightarrow 2NaBr + 2H_2O$

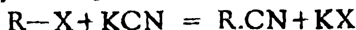
Note :—Hofmann's reaction is used in the conversion of an amide into an amine having ***one atom of carbon less*** than that present in a molecule of an amide. Hence, this reaction is helpful in ***going down the series***, as we shall see it later.

Cyanides or Nitrils.

General formula :—**R—CN** ,
Group radical :—[CN].

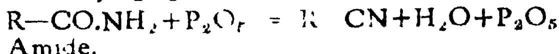
General reaction for the preparation of ***cyanides.***

(1) *Action of an alkyl halide on KCN.*



$$R—X + KCN = R.CN + KX$$

(2) *Action of P_2O_5 on an amide*



$$R—CO.NH_2 + P_2O_5 = R.CN + H_2O + P_2O_5$$

Amide.

Typical cyanide.

Methyl cyanide:—CH_3—CN.

Preparation.

It can be prepared by any of the general methods.

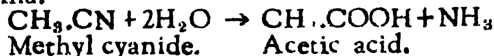
Properties.

Physical.

It is a colourless liquid, possessing ethereal smell. It is soluble in water and in organic solvents.

Chemical.

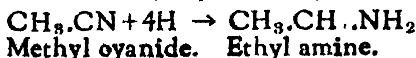
(1) On hydrolysis, it yields acetic acid and ammonia.



$$CH_3.CN + 2H_2O \rightarrow CH_3.COOH + NH_3$$

Methyl cyanide. Acetic acid.

(2) On reduction, it yields ethyl amine.



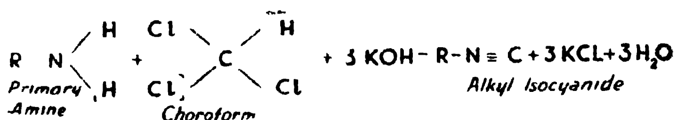
$$CH_3.CN + 4H \rightarrow CH_3.CH_2.NH_2$$

Methyl cyanide. Ethyl amine.

Note :—Alkyl cyanides or nitrils are the compounds, in which the "alkyl" group is attached to a nitrogen atom ***through a carbon atom.*** An alkyl cyanide has an *isomer*, in which the alkyl is attached to a carbon atom ***through a nitrogen atom,*** as for example R—N≡C. This isomer of a cyanide or nitril is known as *iso-cyanide* or *iso-nitril* or ***carbamine*** or ***carbylamine.***

Preparation of alkyl iso-cyanide.

It is prepared by the action of chloroform on a primary amine ($R-NH_2$) in the presence of caustic potash.



Note :—This reaction is also used as a sensitive test for chloroform and also for a primary amine.

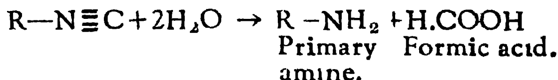
Properties of iso alkyl cyanide.

Physical.

It is a poisonous and colourless heavy liquid, possessing an abnoxious smell.

Chemical.

(1) On hydrolysis, it gives a primary amine and formic acid.



$$R-N\equiv C+2H_2O \rightarrow R-NH_2 + H.COOH$$

Primary amine. Formic acid.

(2) On reduction, it gives a mixed secondary amine.



$$R-N\equiv C+4H \rightarrow R-NH-CH_3$$

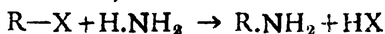
Methyl alkyl amine.
(Mixed secondary amine).

Amines.

General formula :—**R—NH$_2$** ;
Group radical :—**[—NH$_2$]**.

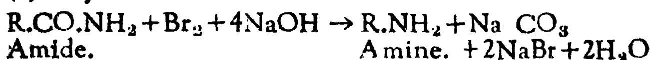
General reactions for the preparation of an amine.

(1) *Action on an alkyl halide on ammonia.*



$$R—X + H.NH_2 \rightarrow R.NH_2 + HX$$

(2) *Hofmann's reaction.*



$$\underset{\text{Amide.}}{R.CO.NH_2} + Br_2 + 4NaOH \rightarrow \underset{\text{Amine.}}{R.NH_2} + Na\ CO_3 + 2NaBr + 2H_2O$$

Typical amine.

Methyl amine :—CH$_3$—NH$_2$.

Preparation.

Twenty five grams of perfectly dry acetamide with a little less amount of bromine is taken in a flask F, kept cool by immersing it in cold water. The flask F is fitted up with a dropping funnel D and a delivery bent tube connected with a receiver, containing dilute HCl, as shown in Fig. 43. About 300 c. c. of a dilute solution of KOH (12% concentration) is introduced into the flask F from the dropping funnel D a little by little, shaking well after each addition, till the solution takes a golden yellow colour. Next a stronger KOH solution is introduced through the dropping funnel. The liquid is carefully heated at constant temperature of

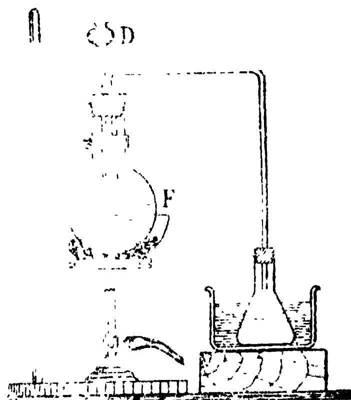


Fig. 43.

70°C for about 30 minutes, after which the liquid is distilled. Methyl amine is evolved in the gaseous form and is absorbed in HCl contained in the receiver. As the acid is evaporated over a water bath, a white residue of methyl amine hydrochloride is obtained in the evaporating basin.

Reaction. [Refer to Hofmann's reaction page 186].

Properties.

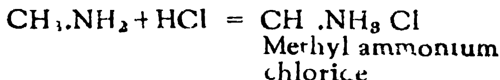
Physical.

Methyl amine is a colourless gas, smelling like ammonia, soluble in water, but it is heavier than air

Chemical.

(1) Methyl amine burns in air with a yellow flame. (*Distinction from ammonia*)

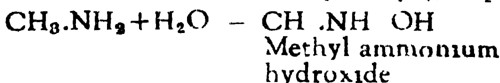
(2) It is more strongly alkaline than ammonia and forms salts with acids as ammonia does.



$$CH_3.NH_2 + HCl = CH_3.NH_3Cl$$

Methyl ammonium chloride

(3) Its solution in water precipitates bases as hydroxides from the solution of salts Methyl amine in solution, therefore, contains a hydroxyl group.



$$CH_3.NH_2 + H_2O = CH_3.NH_3OH$$

Methyl ammonium hydroxide

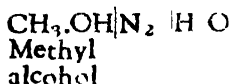
(4) Action of nitrous acid



$CH_3|N\ |H_2$ Methyl amine.



$OH|N\ |O$ Nitrous acid.



$CH_3.OH|N_2\ |H_2O$

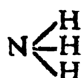
Methyl alcohol

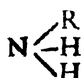
(5) Action of chloroform and caustic potash.

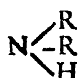
Carbyl amine reaction (page 188), is used as a test for primary amines and also for chloroform.

General study of primary, secondary and tertiary amines

Primary, secondary and tertiary amines may be considered as mono, di or tri "alkyl" derivatives of ammonia.


Ammonia.


Primary amine.

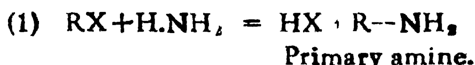

Secondary amine.

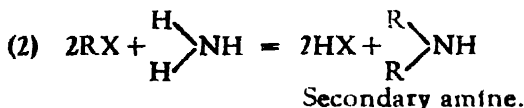

Tertiary amine.

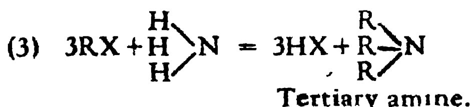
Note :—Methyl amine, already considered in detail is a typical primary amine.

Preparation of secondary and tertiary amines.

Secondary and tertiary amines are generally obtained along with primary, when an alkyl halide is treated with ammonia.


(1) $RX + H.NH_2 = HX + R{-}NH_2$
Primary amine.


(2) $2RX + H_2{>}NH = 2HX + R_2{>}NH$
Secondary amine.


(3) $3RX + H_3{>}N = 3HX + R_3{>}N$
Tertiary amine.

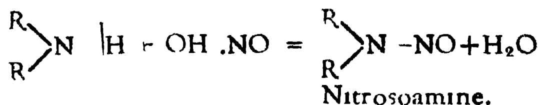
The three amines are, however, separated by Hinsberg's experiment. [Read bottom page 192].

Distinction between primary, secondary and tertiary amines.

(*a*) *Primary amines* on treatment with dil. H_2SO_4 and $NaNO_2$ from an alcohol and evolve nitrogen gas.

Reactions. [Refer to page 69].

(*b*) *Secondary amines* similarly treated produce an oily yellow substance known as nitroso-amine.



$$\frac{R}{R}\!\!>\!N\,\boxed{H + OH}.NO = \frac{R}{R}\!\!>\!N-NO+H_2O$$

Nitrosoamine.

The nitrosoamine so produced is next treated with conc. H_2SO_4 and phenol ($C_6H_5.OH$). The product is diluted immensely and the dilute solution on being made alkaline gives a deep blue or violet coloration. This is a sensitive test for primary amines or for phenol. This sensitive test is known as Liebermann's nitroso test

(c) *Tertiary amines* do not act on nitrous acid.

Carbylamine test.

Only primary amines and also chloroform respond to this test. [Refer to page 188].

Note —Secondary and tertiary amines are without any action on chloroform and caustic potash.

Seperation of primary, secondary and tertiary amines from a mixture of all the three

. This separation is done effectively by Hinsberg's experiment, which is performed as noted :—

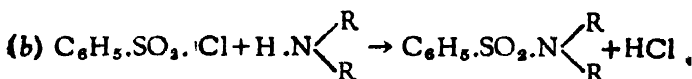
Take the mixture of the three amines and add to it benzene sulphonyl chloride, which acts only on the primary and secondary amines forming sulphonyl derivatives. The tertiary amine does not act on benzene sulphonyl chloride.

Reactions.



$$(a)\ C_6H_5.SO_2.Cl + H.NH.R \rightarrow C_6H_5.SO_2.NH.R + HCl$$

Benzene sulphonyl chloride. P. Amine. Sulphonyl derivative of primary amine.



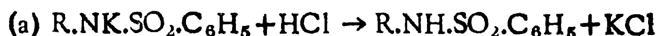
$$(b)\ C_6H_5.SO_2.Cl + H.N\begin{matrix}R\\R\end{matrix} \rightarrow C_6H_5.SO_2.N\begin{matrix}R\\R\end{matrix} + HCl.$$

S. amine. Sulphonyl derivative of secondary amine.

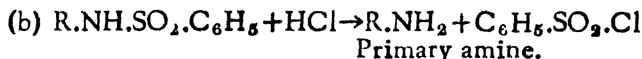
We now thus have a mixture of sulphonyl derivative of primary amine, and that of the secondary amine along with the original tertiary amine. This mixture is next treated with an aqueous solution of caustic potash and we get the potassium sulphonyl derivative of the primary amine, which is very soluble in water. $C_6H_5.SO_2.NH.R + K.OH \rightarrow C_6H_5.SO_2.NK.R + H_2O$. The sulphonyl derivative of the secondary amine and the original tertiary amine are insoluble in water but are soluble in ether. The mixture is transfered to a separating funnel and well agitated with ether. On standing, the aqueous solution of potassium sulphonyl derivative of primary amine separates out and forms the lower layer. The upper layer is the ethereal solution of sulphonyl secondary amine and of the original tertiary amine. On opening the top of the separating funnel, the two layers are separated.

The aqueous layer is hydrolised by dilute hydrochloric acid and we get the sulphonyl derivative of primary amine. The solution is next boiled with conc : HCl and finally distilled with caustic potash. The distillation product is the primary amine.

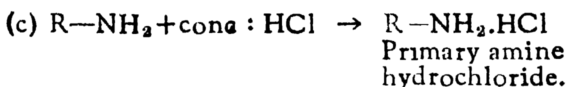
Reactions.



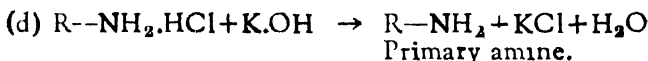
(a) $R.NK.SO_2.C_6H_5 + HCl \rightarrow R.NH.SO_2.C_6H_5 + KCl$



(b) $R.NH.SO_2.C_6H_5 + HCl \rightarrow R.NH_2 + C_6H_5.SO_2.Cl$
Primary amine.



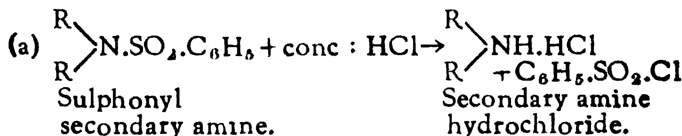
(c) $R{-}NH_2 + conc : HCl \rightarrow R{-}NH_2.HCl$
Primary amine hydrochloride.



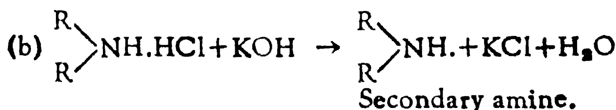
(d) $R{-}NH_2.HCl + K.OH \rightarrow R{-}NH_2 + KCl + H_2O$
Primary amine.

The tertiary amine is separated by subjecting the ethereal solution to fractional distillation and the sulphonyl secondary amine is next converted into the secondary amine by the usual method just described.

Reactions.



(a) $\begin{matrix}R\\R\end{matrix}\!\!>N.SO_2.C_6H_5 + conc : HCl \rightarrow \begin{matrix}R\\R\end{matrix}\!\!>NH.HCl + C_6H_5.SO_2.Cl$
Sulphonyl secondary amine. — Secondary amine hydrochloride.



(b) $\begin{matrix}R\\R\end{matrix}\!\!>NH.HCl + KOH \rightarrow \begin{matrix}R\\R\end{matrix}\!\!>NH. + KCl + H_2O$
Secondary amine.

Acid Chloride.

General formula :— **R—CO—Cl.**

Group radical :— **[—CO—Cl].**

General reaction for the preparation of acid chloride.



$R{-}COOH + PX_5 = R.CO.Cl + HX + POX_3$

Typical acid chloride.

Acetyl chloride $CH_3CO.Cl$.

Preparation.

Fit up an apparatus as shown in Fig. 36, page 171. Introduce 40 grams of perfectly anhydrous acetic acid into the flask DF and 30 grams of phosphorus penta-chloride in the dropping funnel. Add PCl_5 a little by little into the flask and allow it to stand for an hour or so. The acetyl chloride is next distilled over water bath and collected into a receiver provided with an absorption tube containing soda lime.



$$CH_3.COOH + PCl_5 = CH_3.CO.Cl + HCl + POCl_3$$

Acetyl chloride.

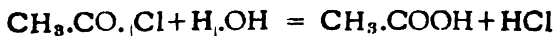
Properties.

Physical.

Acetyl chloride is a volatile, colourless and fuming liquid, possessing an irritating odour. It is heavier than water.

Chemical.

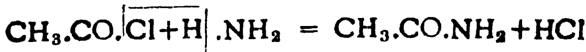
(1) Action of water.



$$CH_3.CO.\boxed{Cl + H}.OH = CH_3.COOH + HCl$$

Acetyl chloride. Acetic acid.

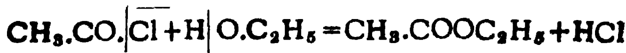
(2) Action of ammonia.



$$CH_3.CO.\boxed{Cl + H}.NH_2 = CH_3.CO.NH_2 + HCl$$

Acetamide.

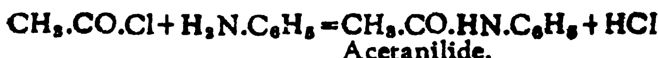
(3) Action of ethyl alcohol.



$$CH_3.CO.\boxed{Cl + H}O.C_2H_5 = CH_3.COOC_2H_5 + HCl$$

Ethyl acetate.

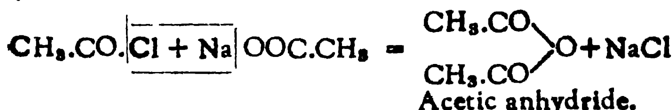
(4) Action of aniline ($C_6H_5.NH_2$)—an aromatic amino compound.



$$CH_3.CO.Cl + H_2N.C_6H_5 = CH_3.CO.HN.C_6H_5 + HCl$$

Acetanilide.

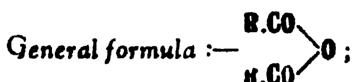
(5) Action of Sodium acetate.



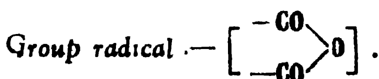
$$CH_3.CO.\boxed{Cl + Na}OOC.CH_3 = \begin{matrix} CH_3.CO \\ CH_3.CO \end{matrix}\!\!>O + NaCl$$

Acetic anhydride.

Acid Anhydride.



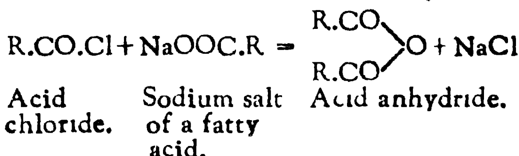
General formula :— $\begin{matrix} R.CO \\ R.CO \end{matrix}\!\!>O$;



Group radical :— $\left[\begin{matrix} -CO \\ -CO \end{matrix}\!\!>O\right]$.

General reaction for their preparation.

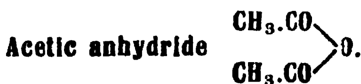
Acid anhydrides are prepared by the action of an acid chloride on sodium salt of a fatty acid.



$$R.CO.Cl + NaOOC.R = \begin{matrix} R.CO \\ R.CO \end{matrix}\!\!>O + NaCl$$

Acid chloride. Sodium salt of a fatty acid. Acid anhydride.

Typical acid anhydride.



Acetic anhydride $\begin{matrix} CH_3.CO \\ CH_3.CO \end{matrix}\!\!>O.$

Preparation.

Sixty grams of fused sodium acetate are taken in a distilling flask DF, fitted up with a dropping funnel and a receiver, which is provided with an absorption tube, containing soda lime, as shown in Fig. 36, page 171 About 50 grams of acetyl chloride are next run down the dropping funnel, a little by little into

the flask DF kept submerged in cold water. Afterwards, the flask is heated over oil bath, and acetic anhydride is collected at about 145°C in the receiver.

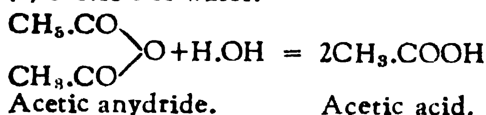
Properties.

Physical.

Acetic anhydride is a colourless liquid, possessing a strong penetrating smell. It is heavier than water.

Chemical.

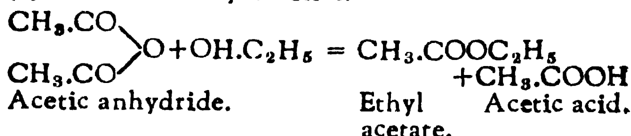
(1) Action of water.



$$\begin{matrix} CH_3.CO \\ CH_3.CO \end{matrix}\!\!>O + H.OH = 2CH_3.COOH$$

Acetic anydride. Acetic acid.

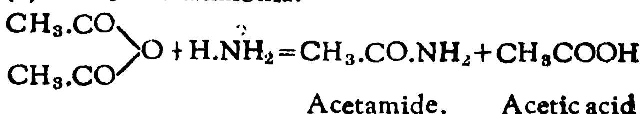
(2) Action of ethyl alcohol.



$$\begin{matrix} CH_3.CO \\ CH_3.CO \end{matrix}\!\!>O + OH.C_2H_5 = CH_3.COOC_2H_5 + CH_3.COOH$$

Acetic anhydride. Ethyl acetate. Acetic acid.

(3) Action of ammonia.



$$\begin{matrix} CH_3.CO \\ CH_3.CO \end{matrix}\!\!>O + H.NH_2 = CH_3.CO.NH_2 + CH_3COOH$$

Acetamide. Acetic acid

Ether.

General formula :—**R—O—R** ;

Group radical :—**[—O—]**.

Note :—*Simple ethers* have both the alkyls *identical*, whereas, *mixed ethers* have both the alkyls *different*.

General reaction for their preparation.



(a) $R—OH + H.HSO_4 = R—HSO_4 + H_2O$



(b) $R—HSO_4 + H.OR = R—O—R + H_2SO_4$
Alcohol. Ether (simple).

Typical ether.

Di-ethyl ether $C_2H_5—O—C_2H_5$.

Preparation.

Fit up an apparatus as shown in Fig. 44. Place 150 c. c. of ethyl alcohol into the flask DF. Add to it about 80 c. c. of strong H_2SO_4, a little by little, shaking well after each addition. Take about 100 c. c. of ethyl alcohol in the dropping funnel. Heat the flask over a sand bath, till the thermometer records 145 C. Allow ethyl alcohol to run down the dropping funnel, a little by little at such a rate as the temperature remains contant at 145°C, at which *ether* condenses and collects (along with water, sulphurous acid and alcohol) into the receiver R which is cooled by cold water. It is purified in a separating funnel in the usual way.

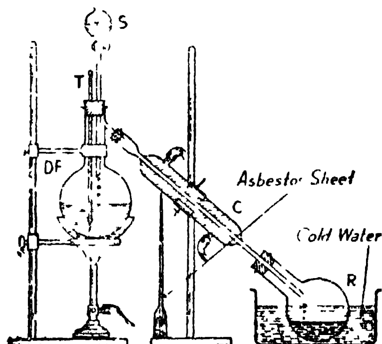


Fig. 44.

Properties

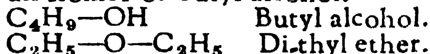
· *Physical.*

Di-ethyl ether is a colourless liquid, possessing a pleasant smell, which is so characteristic of itself. It is slightly soluble in water, but miscible in alcohol. It is a very volatile liquid, and is much lighter than water.

Chemical.

(1) Di-ethyl ether is chemically very inactive.

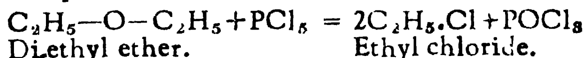
Note :—It is an isomer of butyl alcohol.



$C_4H_9—OH$ Butyl alcohol.
$C_2H_5—O—C_2H_5$ Di-thyl ether.

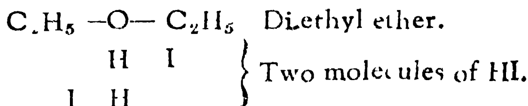
But since, di-ethyl ether has no "hydroxyl group" in its constitution, it shows none of the chemical activities of an alcohol.

(2) Di-ethyl ether, however, reacts with phosphorus penta-chloride.

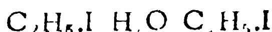


$C_2H_5—O—C_2H_5 + PCl_5 = 2C_2H_5.Cl + POCl_3$
Di-ethyl ether. Ethyl chloride.

(3) Di-ethyl ether is decomposed by hydroiodic acid.



C_2H_5 —O— C_2H_5 Di-ethyl ether.
H I } Two molecules of HI.
I H



$C_2H_5.I$ H_2O $C_2H_5.I$

(4) Di-ethyl ether is highly inflammable and it forms an explosive mixture with air or oxygen.

Note :—Ether being highly inflammable, great care should be taken, that the vapour of ether may not come in contact with a naked flame.

It is therefore, advisible to use in its preparation,

(a) a long condenser,

(b) all air tight connections,

(c) an asbestose sheet between the flame and the receiver, as shown in Fig. 44.

Uses of ether

Ether is used as a solvent for cellulose nitrate, alkaloids and many other organic compounds. It is used in a number of manufacturing processes, such as (a) preparation of collodion (b) explosives (c) artificial silk. Mixed with chloroform, it is used also as an anaesthetic.

Some of the general reactions helpful in the conversion of a compound into a member *(having the same number of carbon atoms)* **of** *a different* **family.**

(1) $R{-}H \xrightarrow{Cl_2} R{-}Cl + HCl$
Hydrocarbon. (Page 51 at the bottom).

(2) $R{-}Cl \xrightarrow{NaOH\ (Aqua)} R{-}OH + NaCl$
Alkyl chloride. Alcohol. (Page 62)

(3) $R{-}Cl \xrightarrow{NaOH\ (Alco)}$ Unsaturated hydrocarbon.
Alkyl chloride. (Page 62 at the bottom).

(4) $R{-}Cl \xrightarrow{NH_3} R{-}NH_2 + HCl$ (Page 63)
Amine.

(5) $R{-}NH_2 \xrightarrow{OH.NO} R{-}OH + N_2 + H_2O$ (Page 69)
Alcohol.

(6) $R{-}CN \xrightarrow{2H_2O} R{-}COOH + NH_3$ (Page 148)
Fatty acid.

(7) $R{-}CN \xrightarrow{4H} R{-}CH_2.NH_2$ (Page 148)
Amine.

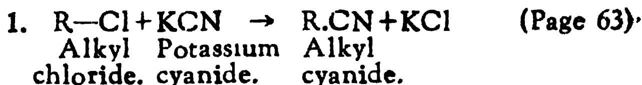
(8) $R{-}OH \xrightarrow{2HI} R{-}H + H_2O + I_2$ (Page 73)
Hydrocarbon.

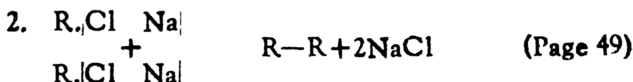
(9) $R.CH_2.OH \xrightarrow{O} R.CHO + H_2O$ (Page 84)
Aldehyde.

(10) $R.CHO \xrightarrow{O} R.COOH$

(11) $\begin{matrix}R\\R\end{matrix}\!\!>C(OH) \xrightarrow{O} \begin{matrix}R\\R\end{matrix}\!\!>C{=}O + H_2O$ (Page 86)
Ketone.

Some of the general reactions helpful during the conversion of a compound into a higher member (*having more number of carbon atoms*) **of** *the same* **or of** *a different* **family.**

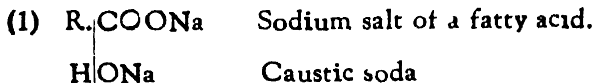




Notes :—1. The reaction No: 1, gives an alkyl cyanide, having one carbon atom *more* than that present in the alkyl chloride, whereas the reaction No: 2, changes a lower alkyl chloride into a higher member of the hydrocarbon.

2. Any one of these two reactions, shall, have to be used at a *suitable* stage during the course of *going up the series*.

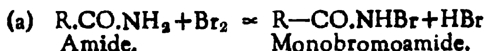
Some of the general reactions helpful during the conversion of a compound into a lower member (*having lesser number of carbon atoms*) **of** *the same* **or of** *a different* **family**





[Refer to page 46).

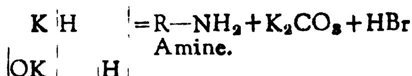
(2) R—CO.NH_2 treated with bromine and caustic potash. [Hofmann's reaction page 186].



(a) $R.CO.NH_2 + Br_2 = R{-}CO.NHBr + HBr$
Amide. Monobromoamide.



(b) $R.CO.NHBr$



KH / OK H $= R{-}NH_2 + K_2CO_3 + HBr$
Amine.

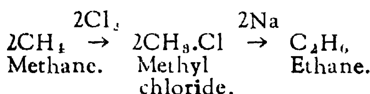
Notes :—1. The reaction No: 1, gives a hydrocarbon, having one carbon atom *less* than that present in the salt of a fatty acid, whereas the reaction No: 2 changes a higher amide into a lower member of an amine.

2. Any one of these two reactions shall have to be used *suitably* during the course of *going down the series.*

Some illustrations of going up and down the series.

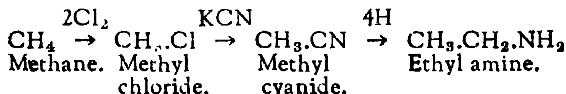
(1) Conversion of methane into ethane and *vice versa*

Going up the series.



$$2CH_4 \xrightarrow{2Cl_2} 2CH_3.Cl \xrightarrow{2Na} C_2H_6$$
Methane. Methyl chloride. Ethane.

(An alternative method).

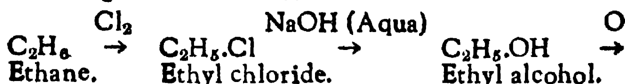


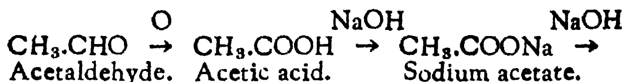
$$CH_4 \xrightarrow{2Cl_2} CH_3.Cl \xrightarrow{KCN} CH_3.CN \xrightarrow{4H} CH_3.CH_2.NH_2$$
Methane. Methyl chloride. Methyl cyanide. Ethyl amine.



$$\xrightarrow{OH.NO} CH_3.CH_2.OH \xrightarrow{2HI} C_2H_6$$
Ethyl alcohol. Ethane.

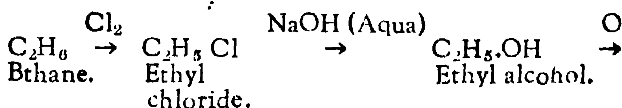
Going down the series.

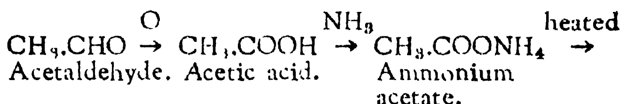


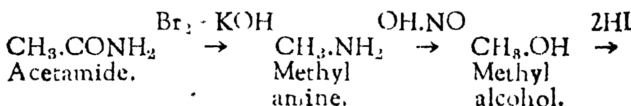




(An alternative method).



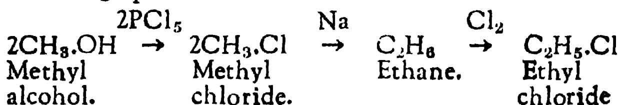


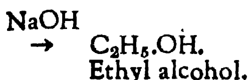




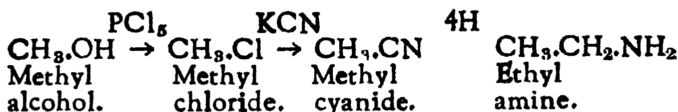
(2) Conversion of methyl alcohol into ethyl alcohol and *vice versa*.

Going up the series.



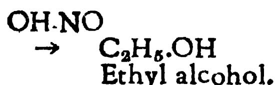


(An alternative method.)



$CH_3.OH \xrightarrow{PCl_5} CH_3.Cl \xrightarrow{KCN} CH_3.CN \xrightarrow{4H} CH_3.CH_2.NH_2$

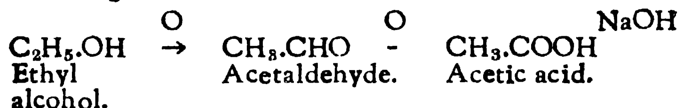
Methyl alcohol. Methyl chloride. Methyl cyanide. Ethyl amine.



$\xrightarrow{OH.NO} C_2H_5.OH$

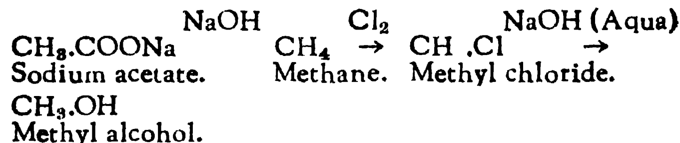
Ethyl alcohol.

Going down the series.



$C_2H_5.OH \xrightarrow{O} CH_3.CHO \xrightarrow{O} CH_3.COOH \xrightarrow{NaOH}$

Ethyl alcohol. Acetaldehyde. Acetic acid.



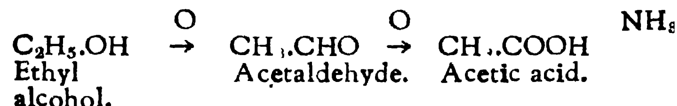
$CH_3.COONa \xrightarrow{NaOH} CH_4 \xrightarrow{Cl_2} CH_3.Cl \xrightarrow{NaOH\ (Aqua)}$

Sodium acetate. Methane. Methyl chloride.

$CH_3.OH$

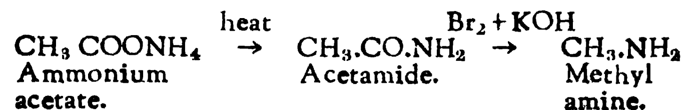
Methyl alcohol.

(An alternative method).



$C_2H_5.OH \xrightarrow{O} CH_3.CHO \xrightarrow{O} CH_3.COOH \xrightarrow{NH_3}$

Ethyl alcohol. Acetaldehyde. Acetic acid.



$CH_3\ COONH_4 \xrightarrow{heat} CH_3.CO.NH_2 \xrightarrow{Br_2 + KOH} CH_3.NH_2$

Ammonium acetate. Acetamide. Methyl amine.

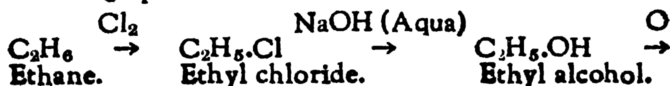


$\xrightarrow{OH.NO} CH_3.OH$

Methyl alcohol.

(3) Conversion of ethane into acetone and *vice versa.*

Going up the series.



$C_2H_6 \xrightarrow{Cl_2} C_2H_5.Cl \xrightarrow{NaOH\ (Aqua)} C_2H_5.OH \xrightarrow{O}$

Ethane. Ethyl chloride. Ethyl alcohol.

$$CH_3.CHO \xrightarrow{O} CH_3.COOH \xrightarrow{Ca(OH)_2}$$

Acetaldehyde. Acetic acid.

$$\begin{matrix} CH_3.COO \\ CH_3.COO \end{matrix} \!\!>\! Ca \xrightarrow{heat} \begin{matrix} CH_3 \\ CH_3 \end{matrix} \!\!>\! C{=}O$$

Calcium acetate. Acetone.

Going down the series.

$$CH_3.CO.CH_3 \xrightarrow{2H} CH_3.CH(OH).CH_3 \xrightarrow{2HI} CH_3.CH_2.CH_3$$

Acetone. Secondary propyl alcohol. Propane

$$\xrightarrow{Cl_2} CH_3.CH_2.CH_2.Cl \xrightarrow{NaOH\ (Aqua)} CH_3.CH_2.CH_2OH$$

Propyl chloride. Primary propyl alcohol.

$$\xrightarrow{O} CH_3.CH_2.CHO \xrightarrow{O} CH_3.CH_2.COOH \xrightarrow{NaOH}$$

Propaldehyde Propionic acid.

$$CH_3.CH_2.COONa \xrightarrow{NaOH} CH_3.CH_3$$

Sodium propionate. Ethane.

(4) Conversion of formic acid into oxalic acid and *vice versa.*

Going up the series.

$$2H.COOH \xrightarrow{NaOH} 2H.COONa \xrightarrow{heat} \begin{matrix} COONa \\ | \\ COONa \end{matrix} \xrightarrow{H_2SO_4} \begin{matrix} COOH \\ | \\ COOH \end{matrix}$$

Formic acid. Sodium formate. Sodium oxalate. Oxalic acid.

Going down the series.

$$\begin{matrix} COOH \\ | \\ COOH \end{matrix} \xrightarrow{Glycerine} H.COOH$$

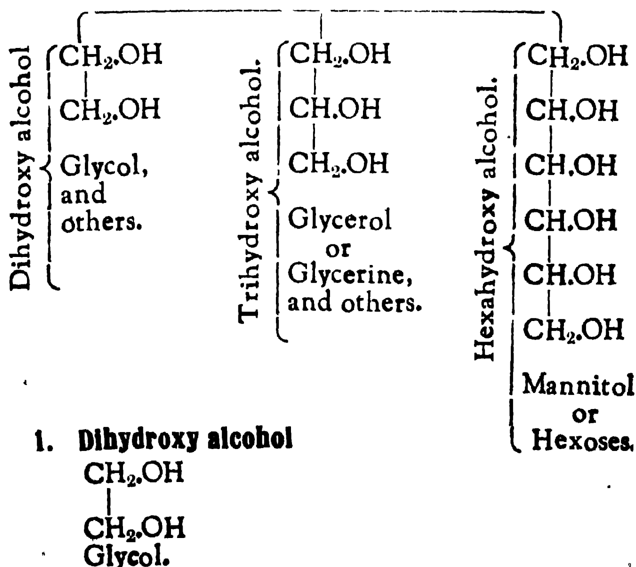
Oxalic acid. Formic acid.

[Read page 154].

CHAPTER X.

Besides the monohydroxy alcohols and their oxidation products discussed in the preceeding chapters, there are also di to hexa hydroxy alcohols. These are called polyhydric alcohols. On oxidation, they are able to give the corresponding aldehydes and polycarboxylic acids. This chapter will be devoted to the study of a few of the polyhydric alcohols, dicarboxylic acids and monohydroxy monocarboxylic or dicarboxylic acids as well as a dihydroxy, dicarboxylic acid. This chapter will also consider urea (carbamide), [a di-amide of carbonic acid] and protiens.

Polyhydric alcohols.



1. Dihydroxy alcohol

$CH_2.OH$
|
$CH_2.OH$

Glycol.

Preparation.

Glycol is prepared by reactions similar to those used in the preparation of monohydroxy alcohols. [Refer to pages 68 and 69].

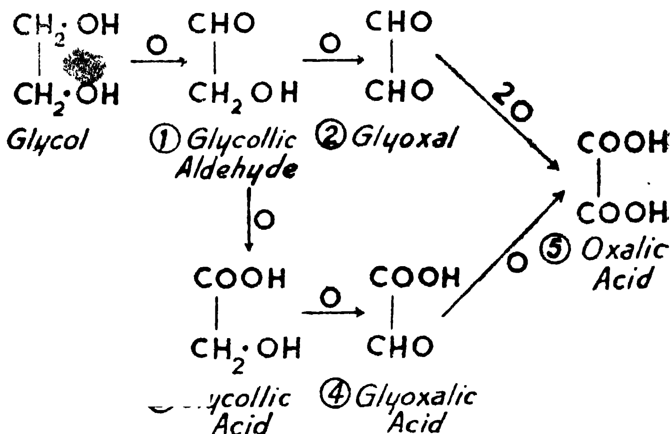
Properties.

Physical.

Glycol is a colourless and odourless thick liquid, possessing sweet taste. It is soluble in water and alcohol; but dissolves with difficulty in ether.

Chemical.

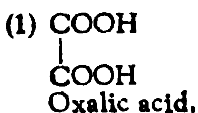
Glycol resembles monohydroxy alcohols in all the properties, in which the reactions of hydroxyl group (—OH) are involved. [Read pages 70 to 78]. Since, glycol contains two (—OH) groups, the reactions will proceed in two stages. Again, since, glycol has two primary alcoholic groups, it yields five oxidation products, as indicated in the following scheme :—

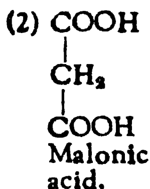


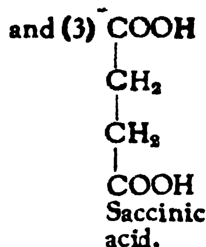
Thus, oxalic acid is the final oxidation product of glycol.

Dicarboxylic acids.

The first three homologues of dicarboxylic acids are :—







1. Oxalic acid

Preparation.

Oxalic acid can be prepared with all the three general methods discussed for the preparption of monocarboxylic acids. [Refer to pages 146 to 148]. Besides these general methods, oxalic acid is conviently prepared in the laboratory by treating cane sugar with strong HNO_3, which is oxidises cane sugar to oxalic acid. When all apparent reactions subside, the solution is evaporated over a water bath, till the bulk is reduced to half. Oxalic acid crystallises out on cooling.

Properties.

Physical.

Oxalic acid is a white crystalline substance, having two molecules of water of crystallisation. It is very poisonous. One gram of it is fatal. Slaked lime taken internally serves as an antidote.

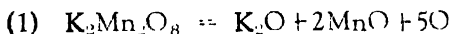
Chemical.

The chemical properties of oxalic acid can be studied by making a reference to the four reactions

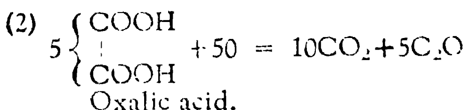
of mono-carboxylic acids, already considered on pages 149 to 153. In addition to these four reactions, the following properties of oxalic acid are very characteristic :—

1. Oxalic acid or an oxalate is a strong reducing agent. It reduces potassium permanganate solution in the presence of dilute H_2SO_4, to a colourless manganous sulphate solution.

Reactions.

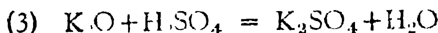


(1) $K_2Mn_2O_8 = K_2O + 2MnO + 5O$

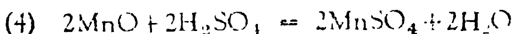


(2) $5\left\{\begin{array}{l} COOH \\ | \\ COOH \end{array}\right. + 5O = 10CO_2 + 5H_2O$

Oxalic acid.



(3) $K_2O + H_2SO_4 = K_2SO_4 + H_2O$



(4) $2MnO + 2H_2SO_4 = 2MnSO_4 + 2H_2O$

2. A solution of oxalic acid, when treated with a solution of calcium chloride, gives a white precipitate of calcium oxalate which is soluble in acetic acid. (*Distinction from tartaric acid*).

3. Oxalic acid or an oxalate, when heated with strong H_2SO_4 in a test tube, evolves a mixture of CO and CO_2, the latter of which is absorbed, by passing the mixture through lime water and the residual CO gas, on ignition burns with a light blue flame as shown in Fig. No: 45.

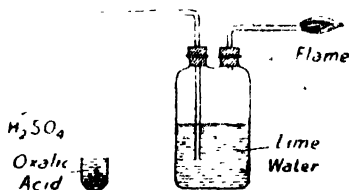


Fig. 45.

4. Oxalic acid or an oxalate on being heated with dilute H_2SO_4 and a little manganesedioxide gives very vigorous effervescence. The effervescence

is generally seen rising up the test tube even after, it is removed from the flame.

Test of oxalic acid.

The above three reactions are used as tests for oxalic acid or for an oxalate.

2. Malonic acid.

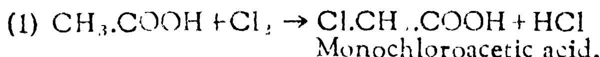
Oxalic acid already studied is the first and malonic acid is the second member of dicarboxylic acids.

The synthesis of malonic acid from carbon and hydrogen, affords a satisfactory evidence for the acceptance of the constitution of the compound as $HOOC.CH_2.COOH$ (malonic acid).

Synthesis of malonic acid from acetic acid.

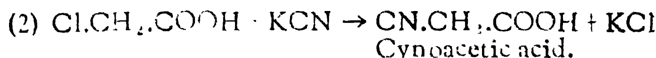
Acetic acid on chlorination yields monochloroacetic acid, which, when treated with potassium cyanide gives cyano-acetic acid. Lastly cyano-acetic acid is hydrolised and we get the malonic acid.

Reactions.



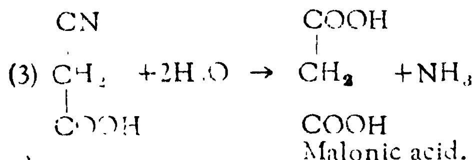
(1) $CH_3.COOH + Cl_2 \rightarrow Cl.CH_2.COOH + HCl$

Monochloroacetic acid.



(2) $Cl.CH_2.COOH + KCN \rightarrow CN.CH_2.COOH + KCl$

Cynoacetic acid.



(3) $\begin{matrix} CN \\ | \\ CH_2 \\ | \\ COOH \end{matrix} + 2H_2O \rightarrow \begin{matrix} COOH \\ | \\ CH_2 \\ | \\ COOH \end{matrix} + NH_3$

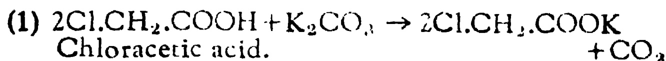
Malonic acid.

Note :—Since acetic acid can be synthesised from its elements, we can synthesis malonic acid starting from carbon and hydrogen through acetic acid.

Preparation.

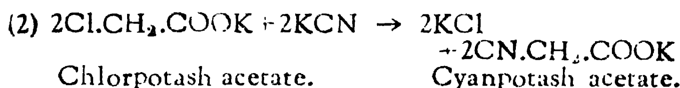
About 100 c. c. of 50% chloroacetic acid solution is neutralized by K_2CO_3. Next, 30 grams of potassium cyanide is added. The mixture is heated in a porcelain basin placed in a fume cupboard. As soon as all reactions have ceased, the mixture is evaporated to dryness over a sand bath.

Reactions.



(1) $2Cl.CH_2.COOH + K_2CO_3 \rightarrow 2Cl.CH_2.COOK + CO_2$

Chloracetic acid.

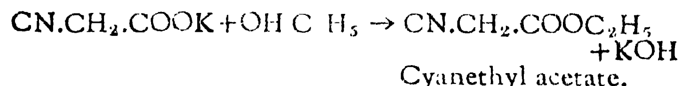


(2) $2Cl.CH_2.COOK + 2KCN \rightarrow 2KCl + 2CN.CH_2.COOK$

Chlorpotash acetate. Cyanpotash acetate.

The residue, which is mainly cyanpotash acetate is po dered and treated with anhydrous ethyl alcohol in the presence of conc: H_2SO_4 in a flask, which is heated over a water bath with a reflux condenser for about three hours.

Reaction.



$CN.CH_2.COOK + OH\,C_2H_5 \rightarrow CN.CH_2.COOC_2H_5 + KOH$

Cyanethyl acetate.

The content of the distilling flask, when cold, is poured into its double the volume of ice cold water. The cyanethylacetate is hydrolised into ethyl malonate which is extracted with ether and separated by fractional distillation.

Properties.

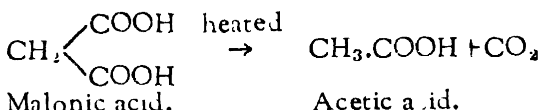
Physical.

Malonic acid is a white and crystalline substance. It is soluble in water.

Chemical.

It is decomposed at 200°C evolving carbondioxide and forming acetic acid.

Reaction.



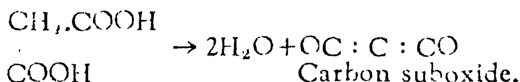
$$CH_2\begin{cases}COOH\\COOH\end{cases} \xrightarrow{\text{heated}} CH_3.COOH + CO_2$$

Malonic acid. Acetic acid.

Note :—All dicarboxylic acids, having both the carboxylic groups attached to the same carbon atom are unstable at 200°C. They are decomposed (if heated alone or in aqueous solution) into carbondi-oxide and a monocarboxylic acid.

Malonic acid, when heated with P_2O_5 yields car-bon suboxide, which is a gas and which acts on water forming malonic acid.

Reaction.

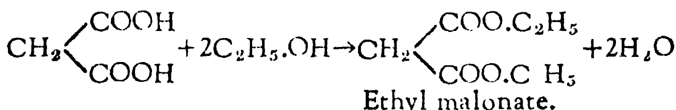


$$\begin{matrix}CH_2.COOH\\ \vert\\ COOH\end{matrix} \rightarrow 2H_2O + OC : C : CO$$

Carbon suboxide.

Malonic acid on being esterified with ethyl alco-hol yields ethyl malonate which is a very important ester used in synthesis of higher homologues of monocarboxylic acids.

Reaction.



$$CH_2\begin{cases}COOH\\COOH\end{cases} + 2C_2H_5.OH \rightarrow CH_2\begin{cases}COO.C_2H_5\\COO.C_2H_5\end{cases} + 2H_2O$$

Ethyl malonate.

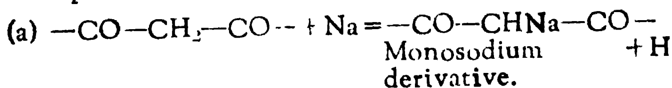
Synthetical importance of ethyl malonate.

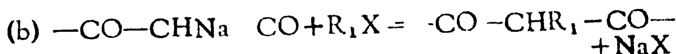
Ethyl malonate affords a convenient method for the synthesis of higher monocarboxylic acids. The importance of this ester in the synthesis of higher fatty acids depends on the characteristic behaviour of $>CH_2$ group in all compounds, when it is pre-sent between two carbonyl groups in the molecule of a compound.

The characteristic behaviour of >CH_2 when between two carbonyl groups (—CO—).

(1) One of the hydrogen atoms of >CH_2 group is replaceable by one atom of sodium, which is next replaced by an alkyl yielding a monoalkyl derivative.

Group reactions.

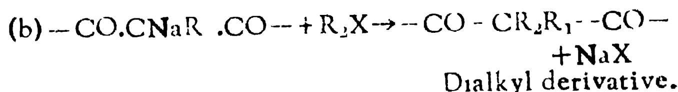

(a) —CO—CH_2—CO— + Na = —CO—CHNa—CO— + H
Monosodium derivative.


(b) —CO—CHNa CO + R_1X = -CO —CHR_1—CO— + NaX

(2) The hydrogen atom in the group >CHR_1 is now replaceable by the next atom of sodium, which in its turn is replaceable in the second installment by an alkyl (similar or dissimilar) yielding a dialkyl derivative.

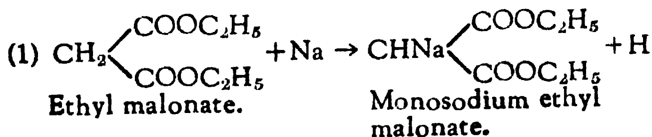
Group reactions.

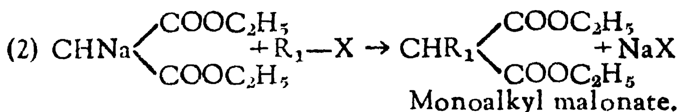

(a) —CO —CHR_1 CO — + Na → —CO -$CNaR_1$—CO— + H


(b) — CO.CNaR .CO— + R_2X → —CO - CR_2R_1 - -CO— + NaX
Dialkyl derivative.

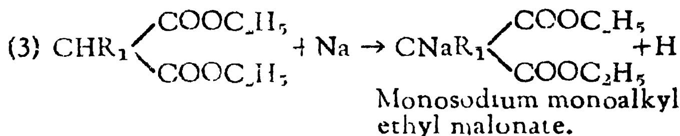
In the constitution of ethyl malonate, we have >CH_2 group between two carbonyl groups and hence, we can follow the reactions step by step in obtaining the dialkyl derivative of the ester.

Reactions with ethyl malonate.

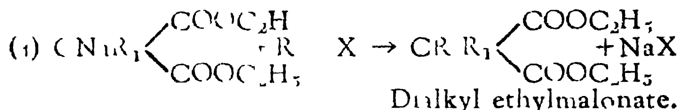

(1) $CH_2<\begin{matrix}COOC_2H_5\\COOC_2H_5\end{matrix}$ + Na → $CHNa<\begin{matrix}COOC_2H_5\\COOC_2H_5\end{matrix}$ + H
Ethyl malonate. Monosodium ethyl malonate.



Monoalkyl malonate.



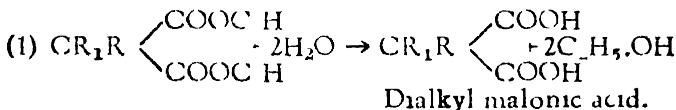
Monosodium monoalkyl ethyl malonate.



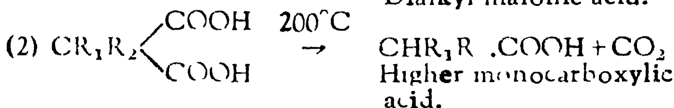
Dialkyl ethylmalonate.

The dialkyl ethyl malonate is next hydrolised and the dialkyl malonic acid so synthesised is heated to 200 C and the higher monocarboxylic acid is obtained.

Reactions.



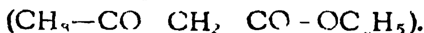
Dialkyl malonic acid.



Higher monocarboxylic acid.

Like ethylmalonate, there is ethylacetoacetate, another ester of monocarboxylic acid, helpful in the synthesis of not only higher fatty acids but also of higher ketones. It will, therefore, be convenient to study ethylacetoacetate at this stage.

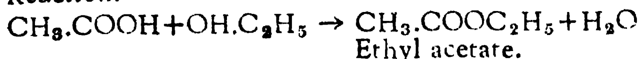
Ethylaceto acetate



Synthesis of ethylaceto acetate from acetylene.

We have seen that acetic acid can easily be synthesised from acetylene. The acetic acid, when esterified with ethyl alcohol yields ethyl acetate.

Reaction.

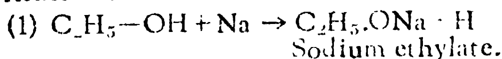


$$CH_3.COOH + OH.C_2H_5 \rightarrow CH_3.COOC_2H_5 + H_2O$$

Ethyl acetate.

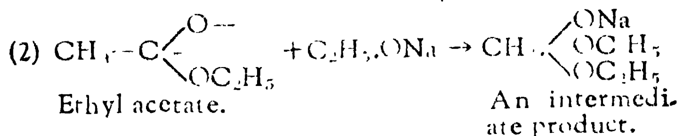
The ethyl acetate is treated with sodium drawn into a wire in the presence of ethyl alcohol in a flask fitted up with reflux condenser. The flask is heated over a water bath, until the entire amount of sodium has acted yielding the sodium derivative of ethylacetoacetate as a thick brown semi-solid product. The following reactions take place :-

Reactions.



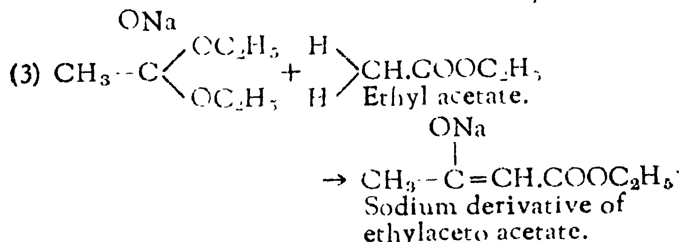
(1) $C_2H_5-OH + Na \rightarrow C_2H_5.ONa + H$

Sodium ethylate.



(2) $CH_3-C \begin{cases} O \\ OC_2H_5 \end{cases} + C_2H_5.ONa \rightarrow CH_3.C \begin{cases} ONa \\ OC_2H_5 \\ OC_2H_5 \end{cases}$

Ethyl acetate. An intermediate product.



(3) $CH_3-C(ONa) \begin{cases} OC_2H_5 \\ OC_2H_5 \end{cases} + \begin{matrix} H \\ H \end{matrix} \rangle CH.COOC_2H_5$

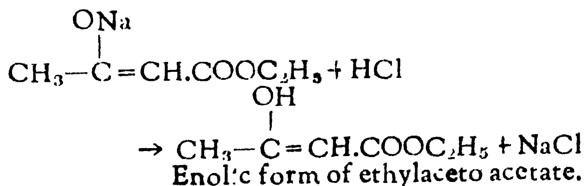
Ethyl acetate.

$\rightarrow CH_3-C(ONa)=CH.COOC_2H_5$

Sodium derivative of ethylaceto acetate.

The sodium derivative is next hydrolised with dilute hydrochloric acid and we get the *enolic* form of ethylacetoacetate.

Reaction.

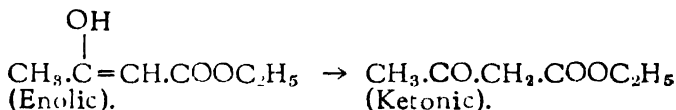


$$CH_3-C(ONa)=CH.COOC_2H_5 + HCl$$

$$\rightarrow CH_3-C(OH)=CH.COOC_2H_5 + NaCl$$

Enolic form of ethylaceto acetate.

In the acidic solution, the enolic form undergoes a *tautomeric change*, in which the hydrogen atom from the hydroxyl group jumps to the adjacent double linked carbon atom. The *enolic* form is thus changed into *ketonic* form.



$$CH_3.\overset{\overset{OH}{|}}{C}=CH.COOC_2H_5 \rightarrow CH_3.CO.CH_2.COOC_2H_5$$

(Enolic). (Ketonic).

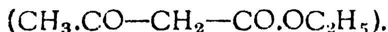
Ordinarily, the ethylacetoacetate exists entirely in the ketonic form with a small proportion of enolic form. The ester, however, is capable of conversion of one form into the other under the influence of the various reagents. Such isomerism in which the isomers are rapidly changing one into the other (involving the pump of H atom) is known as *tautomeric* or *dynamic* isomerism. A mixture of enolic and ketonic forms in equilibrium is called *allelotropic mixture*.

Enolic → Ketonic.

In the presence of an acid, the enolic form in the allelotropic mixture is changed into ketonic form. But in the presence of metallic sodium or sodium ethylate, the ketonic form, is changed back to the enolic form.

Synthetical importance of ethylaceto acetate.

Ethylaceto acetate.



$$(CH_3.CO—CH_2—CO.OC_2H_5).$$

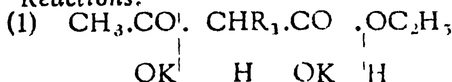
In the constitution of this ester, we find again that the group $>CH_2$ is between two carbonyl groups, as it was in the case of ethyl malonate. Hence, ethylaceto acetate also is capable to give its mono or dialkyl derivatives.

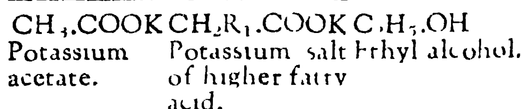
The mono or dialkyl ethylacetoacetate is subjected to the acidic or ketonic hydrolysis for the synthesis of higher fatty acids or higher ketones respectively.

(1) *Acidic hydrolysis of an alkyl derivative of ethylacetoacetate.*

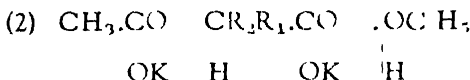
The alkyl derivatives of ethylacetoacetate, when treated with a strong alcoholic potash undergo acidic hydrolysis and yield a mixture of potassium salt of higher fatty acid with potassium acetate and ethyl alcohol.

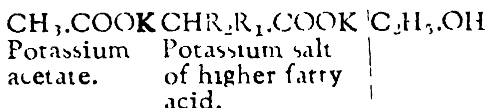
Reactions.





or

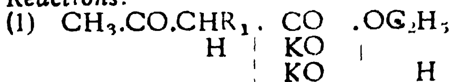


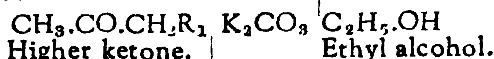


(2) *Ketonic hydrolysis of ethylaceto acetate.*

A boiling dilute solution of potassium hydroxide brings about ketonic hydrolysis of the alkyl derivatives of ethylacetoacetate yielding potassium carbonate and a mixture of higher ketone with ethyl alcohol.

Reactions.

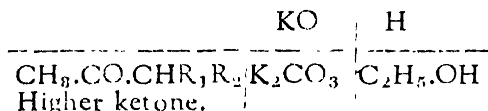




or,



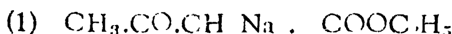


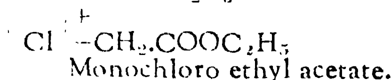


(3) *Synthesis of succinic acid from the monosodium derivatives of ethylaceto acetate.*

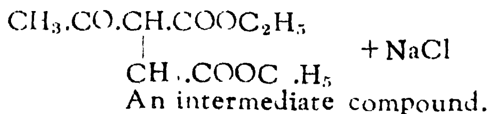
Monosodium ethylacetoacetate is treated with monochloro-ethylacetate. The intermediate compound formed on hydrolysis yields a mixture of potassium acetate, potassium succinate and ethyl alcohol.

Reactions.

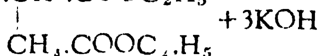


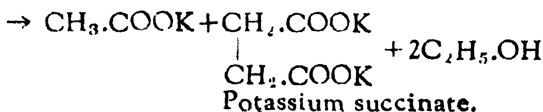




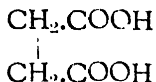






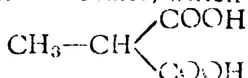


3. Succinic acid.



$$\begin{array}{l} CH_2.COOH \\ | \\ CH_2.COOH \end{array}$$

This is the third member of dicarboxylic acids. Succinic acid has an *isomer*, which is represented as



$$CH_3—CH\begin{cases} COOH \\ COOH \end{cases}$$

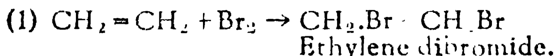
This isomer of succinic acid is known as isosuccinic acid.

Synthesis of succinic acid.

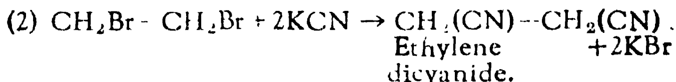
It may be synthesised from (1) ethyl acetoacetate as already described on page 218 or (2) ethylene in the following way.

Ethylene on being brominated gives ethylene dibromide, which can readily be converted into ethylene dicyanide. The ethylene dicyanide on hydrolysis yields succinic acid.

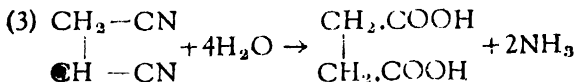
Reactions.



(1) $CH_2 = CH_2 + Br_2 \rightarrow CH_2.Br - CH_2Br$
Ethylene dibromide.



(2) $CH_2Br - CH_2Br + 2KCN \rightarrow CH_2(CN) - CH_2(CN) + 2KBr$
Ethylene dicyanide.



(3) $$\begin{array}{l} CH_2—CN \\ | \\ CH_2—CN \end{array} + 4H_2O \rightarrow \begin{array}{l} CH_2.COOH \\ | \\ CH_2.COOH \end{array} + 2NH_3$$

Both the synthetical reactions involved in the synthesis of succinic acid prove its constitution.

Properties

Physical.

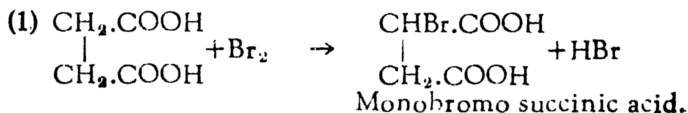
It is a white crystalline solid. It melts at 120°C and is soluble in water.

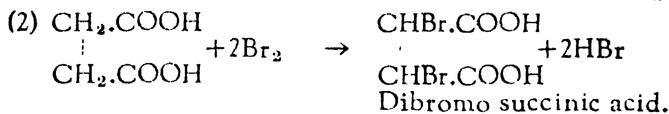
Chemical.

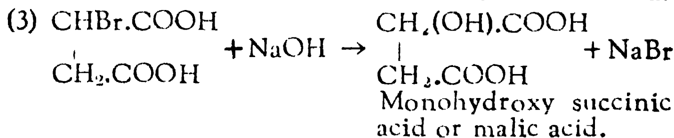
(1) Its behaviour towards various reagents is the same as that of monocarboxylic acids in yielding salts, esters, acid chlorides, amides and anhydrides.

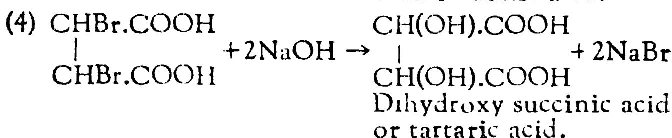
(2) On being chlorinated or brominated it yields mono and di-substitution products, which when treated with aqueous caustic soda or potash give mono or dihydroxy dicarboxylic acids.

Reactions.

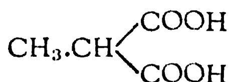








Isosuccinic acid.

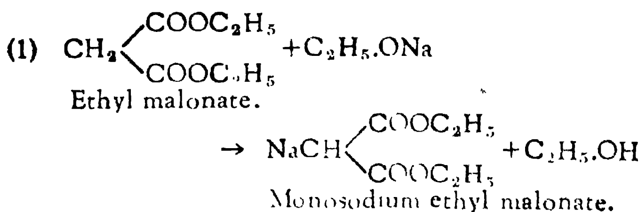


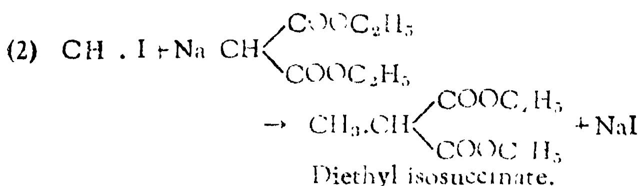
It is an isomer of succinic acid.

Synthesis of isosuccinic acid.

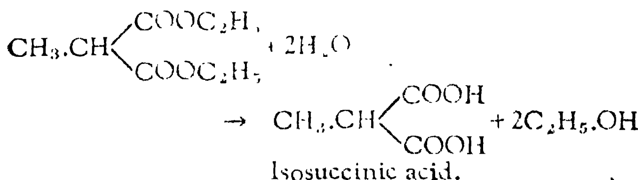
Ethyl malonate when treated with sodium ethylate yields monosodium ethyl malonate, which, when treated with methyl iodide yields di-ethyl isosuccinate.

Reactions.





The diethyl isosuccinate on hydrolysis yields iso. succinic acid.



The above synthesis affords a satisfactory evidence of the constitution of isosuccinic acid. The isosuc. cinic acid differs from succinic acid in its being unstable at 200°C at which it decomposes and gives propionic acid and CO_2 exactly as malonic acid yields CO_2 along with acetic acid.

Monohydroxy monocarboxylic acids.

There are two important monohydroxy monocar. boxylic acids, namely :—

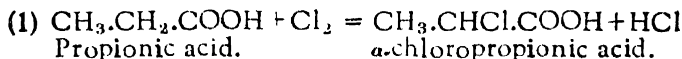
(1) Lactic acid or α.hydroxy propionic acid.

(2) Hydrocrylic acid or β.hydroxy propionic acid.

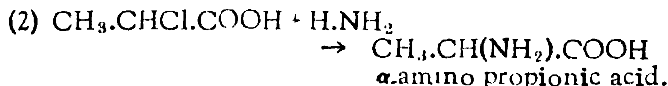
Both these acids may be considered as **derivatives** of propionic acid.

The mono-chlorination product of propionic acid may be α-chloropropionic acid or β-chloropropionic acid, which when treated with ammonia would yield respectively α-amino or β-amino propionic acid. These amino derivatives on treatment with nitrous acid give lactic or hydrocrylic acid.

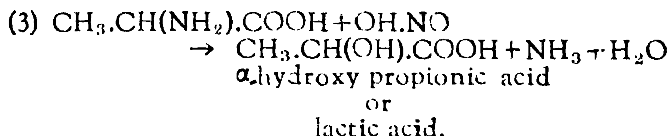
Reactions.



(1) $CH_3.CH_2.COOH + Cl_2 = CH_3.CHCl.COOH + HCl$
Propionic acid. α-chloropropionic acid.



(2) $CH_3.CHCl.COOH + H.NH_2 \rightarrow CH_3.CH(NH_2).COOH$
α-amino propionic acid.



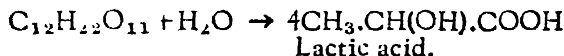
(3) $CH_3.CH(NH_2).COOH + OH.NO \rightarrow CH_3.CH(OH).COOH + NH_3 + H_2O$
α-hydroxy propionic acid
or
lactic acid.

Again substituting a chlorine atom in β-position of the propionic acid, we shall get β-chloropropionic acid, from which we can easily derive β-hydroxy propionic acid or hydrocrylic acid [$CH_2(OH).CH_2.COOH$].

Lactic acid or (*α-hydroxy propionic acid*).

It is prepared by the fermentation of milk sugar present in milk, when it is exposed to air. The *lactic ferments* present in air fall on milk and set up lactic fermentation during which milk sugar ($C_{12}H_{22}O_{11}$) present in milk is hydrolysed and is changed into lactic acid, which tastes sour.

Reaction.



$C_{12}H_{22}O_{11} + H_2O \rightarrow 4CH_3.CH(OH).COOH$
Lactic acid.

Properties.

(1) Lactic acid in the presence of decaying cheese undergoes *butyric fermentation* and is changed into butyric acid by butyric ferments present in the decaying cheese.

Reaction.



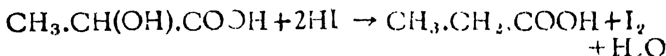
$$2CH_3.CH(OH).COOH \rightarrow \underset{\text{Butyric acid.}}{CH_3.CH_2.CH_2.COOH} + 2CO_2 + 2H_2O$$

(2) Lactic acid has in its constitution a —COOH as well as a secondary alcoholic group. Hence, it behaves towards various reagents as a carboxylic acid and also as a secondary alcohol.

(a) It forms salts with bases and yields esters with alcohols

(b) It is reduced with HI to propionic acid.

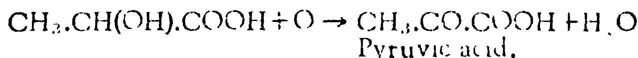
Reaction.



$$CH_3.CH(OH).COOH + 2HI \rightarrow CH_3.CH_2.COOH + I_2 + H_2O$$

(c) It is oxidised to pyruvic acid with potassium permanganate.

Reaction.

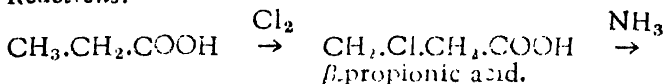


$$CH_3.CH(OH).COOH + O \rightarrow \underset{\text{Pyruvic acid.}}{CH_3.CO.COOH} + H_2O$$

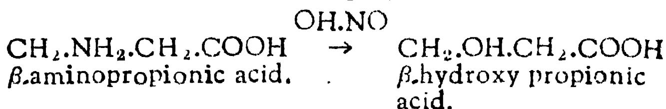
Hydracrylic acid (*or β-hydroxy propionic acid*).

β-hydroxy propionic acid [$CH_2.(OH).CH_2.COOH$] is obtained by reactions already considered for the preparation of α-hydroxy propionic acid.

Reactions.



$$CH_3.CH_2.COOH \xrightarrow{Cl_2} \underset{\beta\text{-propionic acid.}}{CH_2.Cl.CH_2.COOH} \xrightarrow{NH_3}$$



$$\underset{\beta\text{-aminopropionic acid.}}{CH_2.NH_2.CH_2.COOH} \xrightarrow{OH.NO} \underset{\beta\text{-hydroxy propionic acid.}}{CH_2.OH.CH_2.COOH}$$

Properties.

(1) As hydracrylic acid contains a primary alcoholic group —$CH_2.OH$ besides a carboxylic group, it is readily oxidised with chromic acid to malonic acid, which (as we have already seen on page 210), is the second member of dicarboxylic acid.

Reaction.

$$\underset{\text{Hydracrylic acid.}}{CH_2.(OH).CH_2.COOH} + 2O \rightarrow \underset{\text{Malonic acid.}}{HOOC.CH_2.COOH} + H_2O$$

(2) Hydracrylic acid on being treated with sulphuric acid gives an unsaturated monocarboxylic acid known as ***acrylic acid.***

Reactions.

(a) $CH_2.OH.CH_2.COOH + H.HSO_4$
$\rightarrow CH_2.HSO_4.CH_2.COOH + H_2O$

(b) $CH_2.HSO_4.CH_2\,COOH \rightarrow \underset{\text{Acrylic acid.}}{CH_2{=}CH.COOH} + H_2SO_4$

Synthesis of lactic acid.

Acetylene is synthetically obtained by passing a high voltage electric current between two carbon

Fig. 46.

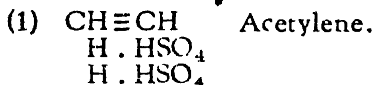
electrodes in a bulb, through the one end of which hydrogen gas is passed as shown in Fig. 46. The acetylene gas comes out through the other end.

Reaction.

$$2C+2H \rightarrow CH{\equiv}CH.$$

Acetylene gas, when passed into about 20% sulphuric acid in the presence of mercuric sulphate, is hydrolised to acetaldehyde.

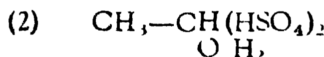
Reactions.



(1) $CH \equiv CH$ Acetylene.
$H \cdot HSO_4$
$H \cdot HSO_4$



$CH_3 \quad CH(HSO_4)_2$



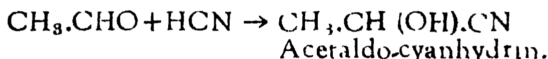
(2) $CH_3—CH(HSO_4)_2$
$O \; H_2$



$CH_3 -CHO \; 2H_2SO_4$
Acetaldehyde.

The acetaldehyde so synthesised, is next treated with hydrocyanic acid and we get acetaldocyanhydrin.

Reaction.



$CH_3.CHO + HCN \rightarrow CH_3.CH(OH).CN$
Acetaldo-cyanhydrin.

The acetaldo-cyanhydrin on hydrolysis yields lactic acid.

The study of the reactions involved in the synthesis of lactic acid throws light on its constitution and proves that the molecule of lactic acid has the hydroxyl group in α-position with respect to COOH group of the propionic acid.

Synthesis of hydrocrylic acid.

Starting with carbon and hydrogen, we can obtained acetylene, which on reduction gives ethylene. Ethylene is next treated with hypochlorous acid and is converted into monochloroglycol. The monochloroglycol on treatment with KCN forms monocyanoglycol. The monocyanoglycol on hydrolysis yields β-hydroxypropionic acid or hydrocrylic acid.

Reactions.

(1) $2C+2H=HC\equiv CH$ Acetylene.

(2) $CH\equiv CH+2H \rightarrow CH_2=CH_2$ Ethylene.

(3) $CH_2=CH_2+HOCl \rightarrow CH_2(OH).CH_2.Cl$.

(4) $CH_2(OH).CH_2Cl+KCN \rightarrow CH_2.OH.CH_2.CN+KCl$

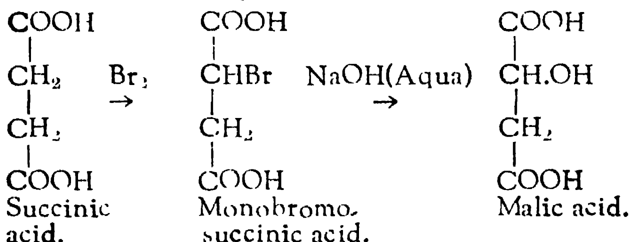
(5) $CH_2(OH).CH_2.CN+2H_2O \rightarrow CH_2(OH).CH_2.COOH + NH_3$

β-hydroxy propionic acid or hydrocrylic acid.

The reaction involved in the synthesis of hydrocrylic acid throw light on its constitution and proves that a molecule of the acid has the hydroxyl group in β-position with respect to —COOH group of the propionic acid.

Monohydroxy dicarboxylic acid.

Malic acid [a representative member of monohydroxy dicarboxylic acids] is derived from succinic acid as studied on page 220.



Succinic acid. Monobromo-succinic acid. Malic acid.

Properties.

Physical.

It is a hite crystalline deliquescent solid soluble in water and alcohol.

Chemical.

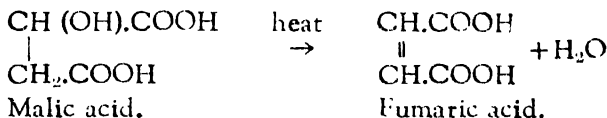
From the consideration of the constituion of malic acid, its chemical behaviour can be predicated.

It will behave as a carboxylic acid as well as a secondary alcohol. When heated, malic acid, however, undergoes remarkable changes.

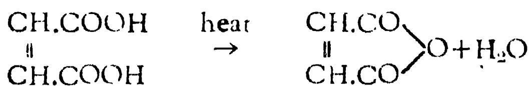
Effect of heat on malic acid.

When heated, it does not form an anhydride as succinic acid does. But it forms an unsaturated dicarboxylic acid known as fumaric acid.

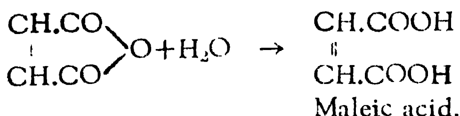
Reaction.



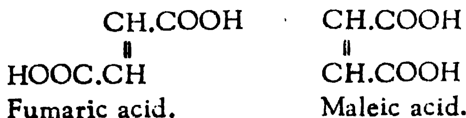
Next, when fumaric acid is heated, a part of it forms anhydride called maleic anhydride.



Maleic anhydride when boiled with water yields maleic acid which is an isomer of fumaric acid.



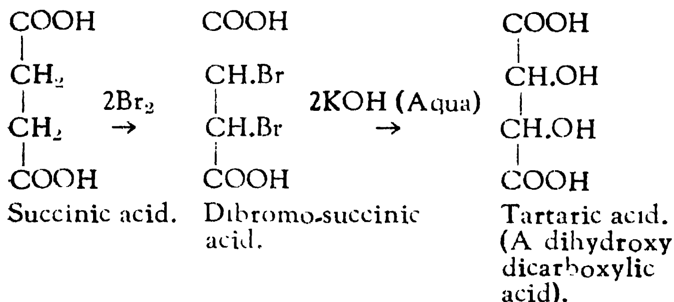
Since maleic acid forms its anhydride and fumaric acid generally does not, the constitution of both are different due to the different distribution of —COOH group in space as shown below :—



[Read Stereoisomerism on page 232].

Dihydroxy dicarboxylic acid.

Tartaric acid, [a representative member of dihydroxy dicarboxylic acids] is derived from succinic acid as we have already studied on page 220.



Properties.

Physical.

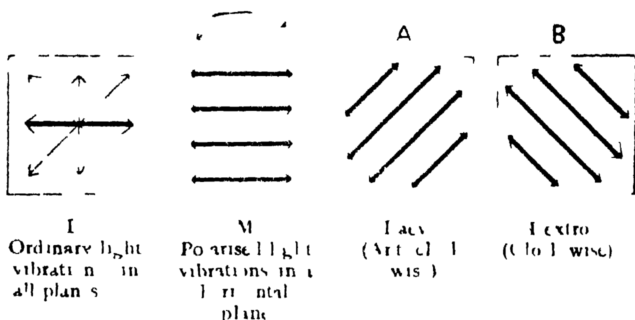
(1) It is a white crystalline solid, possessing very sour taste.

(2) Its solution is optically active.

Note :--Optically active substances are those which in liquid form or in solution are able to rotate the plane of *polarised light*.

Polarised light

The propagation of light is a transverse wave motion. Transverse vibrations are executed in innumerable planes, simultaneously. Thus the propagation of ordinary light rays is due to the transverse vibrations in all possible planes as shown in L, on next page.



I
Ordinary light vibration in all planes

M
Polarised light vibrations in horizontal plane

Laevo (Anticlockwise)

Dextro (Clockwise)

If a beam of ordinary light is passed through a certain crystal—say Iceland spar known as "Nicol prism", the beam emerges out of the prism as a *polarised light* as it now consists of *vibrations in only one plane*. The prism cuts off the vibrations executed in every other plane except *one*. Thus, a polarised light differs from ordinary white light in consisting of transverse vibrations of *only one* plane. Substances (solids, liquids or solutions), which are able to rotate the plane of polarised light to the right (clock-wise) or to the left (anticlock-wise) are optically active. [Refer to the sketches B and A above.]

Tartaric acid *in solution* is optically active. In the light of optical activity, we are familiar with four forms of tartaric acid.

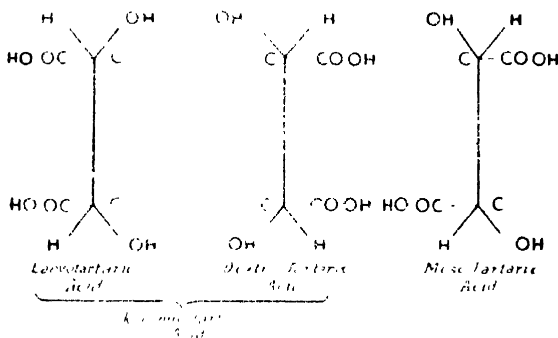
1. **Dextrotartaric** is the variety of the acid, which is able to rotate the plane of polarised light to the right (clock-wise).

2. **Laevotartaric** is the variety of the acid, which is able to rotate the plane of polarised light to the left (anti-clockwise).

3. **Racemictartaric** is the variety of the acid, which is a mixture of dextro and laevo in the

equimolecular proportion ; and thus it is apparently optically inactive, due to the ***external compensation.***

4. **Mesotartaric** is the variety of the acid, in which half the molecule, is dextro, and the other half is equally laevo. This variety is also apparently optically inactive ; but it is due to the ***internal compensation.***



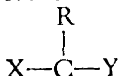
Note :—All these different varieties of tartaric acid are chemically identical, as we shall see it later, under the chemical properties of tartaric acid. They differ, however, in their crystalline structure and in their effect on the plane of polarised light, when they are in solution.



J. H. VAN'T HOFF.

In 1874, Van't Hoff and Le Bel advanced a theory according to which, it is assumed :—

(1) that the property of optical activity a of a carbon compound is due to the presence in its molecule of at least one carbon atom which is **asymmetrical**. An **asymmetrical crabon** atom has each of its four bonds united with four *different* atoms or groups, as for example



(2) that every carbon atom in the constitution of a carbon compound is situated at the centre of an *imaginary* regular **tetrahedron,**

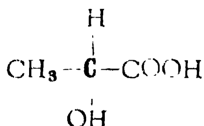
(3) and that each of the four bonds of the carbon atom is acting in the direction from the centre of the tetrahedron to its four corners and to each of which a monovalent atom or group is attached as **distrtbuted in space**.

The study of dextro and laevo forms of tartaric acid leads to a new type of isomerism called space isomerism or stereoisomerism.

Development of stereoisomerism.

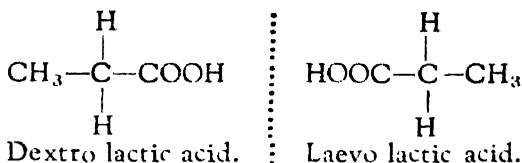
Tartaric acid as obtained from grape juice was found to be dexro. But the acid obtained from the mother liquor of the grape juice after separation of the dextro, was found to be optically inactive. This acid was called racemic tartaric acid. The sodium salt of racemic acid on microscopic examination revealed, that it was a mixture of two kinds of salts having different crystalline shapes, which were related to one another, as an object is related to its image. Pasteur separated both the varieties of salt and dissolved them separately. On placing these solutions into the path of the polarised light, one was found to be dextro rotatory, while the other laevo to the same extent. Equal volumes of both these solutions, when mixed, were found to be optically inactive. Thus racemic tartaric acid is shown to be the mixture of dextro and laevo.

Lactic acid already studied on page 222 in an optically active substance as it has **one asymmetrical carbon atom**



Lactic acid.

Since any compound, in which there is at least *one* carbon atom attached to four *different* atoms or groups, can exist in two and *only two* such forms, as may be related to one another, as an object is related to its image, lactic acid is capable to exist in two isomeric forms dextro and laevo, having identical chemical properties, but having different effect on the *polarised* light due to the difference in the distribution of the atoms or groups in space.



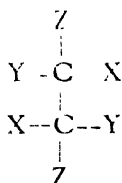
Such an isomerism of space is known as stereo-isomerism.

A mixture of these two stereoisomeric lactic acids in equal proportions will be apparently optically inactive due to the external compensation.

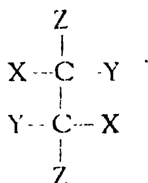
In the constituion of tartaric acid, if we take X=H, Y=OH, Z=-COOH, R= CH.(OH).COOH we shall see that a molecule of tartaric acid has ***two asymmeirical*** carbon atoms.

According the theory of Van't Hoff and Le Bel, we know that X, Y, Z and R may be distributed in space so differently as to have three models No: 1, No: 2 and No: 3 to represent the stereoisomeric forms of tartaric acid.

Model No: I.



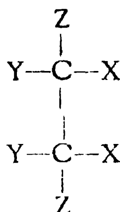
Model No: II.



The molecules of tartaric acid represented by model No: II, is a mirror image of the molecule represented by the model No: I. Thus if the tartaric acid represented by the model No: I is dextro, that represented by the model No: II must to laevo. If we consider a mixture of both in equimolecular proportion we shall have an apparently optically inactive form of tartaric acid as due to the external

compensation. This stereoisomeric form of tartaric acid is known as racemic variety.

Model No: III.



Half of the molecule of tartaric acid as represented by the model No: III is a mirror image of the other half. Hence, if half of the molecule of such a variety of tartaric acid is dextro, the other half of the molecule will be laevo equally. The molecule of this stereoisomer of tartaric acid will, therefore, be optically inactive as due to the internal compensation.

This stereoisomer of tartaric acid is known as mesotartaric acid.

Chemical properties of tartaric acid.

Tartaric acid will give the reactions of carboxylic acid and that of secondary alcohols, in two stages, since tartaric acid contains in its constitution two secondary alcoholic groups and two carboxylic groups. Besides these, the following reactions of tartaric acid are very characteristic.

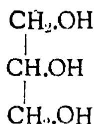
1. It is able to reduce ammonical solution of silver nitrate to metallic silver.

2. It is charred, when treated with strong H_2SO_4.

3. Calcium chloride solution, gives a white precipitate, with a neutral solution of tartaric acid. The white precipitate is soluble in acetic acid. *(Distinction from oxalic acid).*

2 Trihydroxy alcohol.

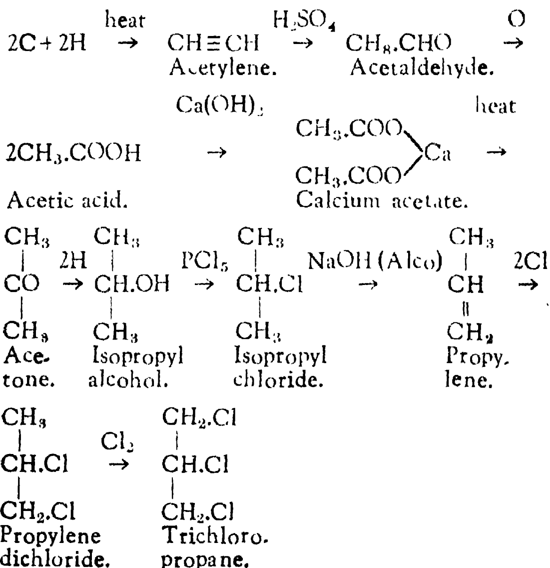
Glycerine



Glycerine or glycerol.

Synthesis of glycerine or glycerol.

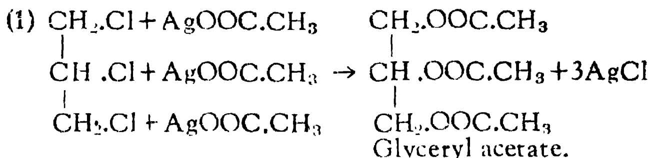
Synthetical reactions of glycerine or glycerol are shown below :--



The trichloropropane, thus synthesised, is next treated with silver acetate and we get glyceryl ace-

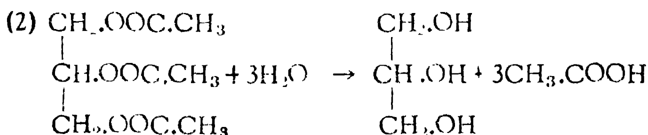
tate, which on being hydrolised yields glycerine or glycerol.

Reactions.



$$(1)\quad \begin{matrix} CH_2.Cl + AgOOC.CH_3 \\ | \\ CH\ .Cl + AgOOC.CH_3 \\ | \\ CH_2.Cl + AgOOC.CH_3 \end{matrix} \rightarrow \begin{matrix} CH_2.OOC.CH_3 \\ | \\ CH\ .OOC.CH_3 \\ | \\ CH_2.OOC.CH_3 \end{matrix} + 3AgCl$$

Glyceryl acetate.



$$(2)\quad \begin{matrix} CH_2.OOC.CH_3 \\ | \\ CH.OOC.CH_3 \\ | \\ CH_2.OOC.CH_3 \end{matrix} + 3H_2O \rightarrow \begin{matrix} CH_2.OH \\ | \\ CH\ .OH \\ | \\ CH_2.OH \end{matrix} + 3CH_3.COOH$$

Manufacture of glycerine

Glycerine is manufactured from "**spent lye**" obtained from the saponifying tank, after salting out of the soap. [Read at the bottom page 180].

The "spent lye", contains alkali along with some fatty acids and glycerine. The alkali is neutralised by calculated amount of HCl. The fatty acids are saponified with ferric sulphate and is precipitated as iron soap in the treating tank Fig. 46. The gelatinous iron soap and brown ferric hydroxide settle down in the treating tank. A neutral solution

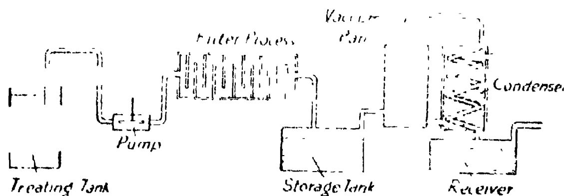


Fig. 46.

of giycerine is pumped up the treating tank, through a filter press, which removes the precipitates of iron

soap and ferric hydroxide. The filtrate from the filter press is collected in a storage tank wherefrom, it is led to a vacuum pan, which is connected with an exhaust pump (not shown in Fig. 46). As the pump works, the pressure in the vacuum pan is considerably reduced and water is boiled off—the steam condenses in the cooling tank and collects in the receiver. The glycerine remaining in the vacuum pan, still contains some water and colouring matter. The colouring matter is removed by filtration of the crude glycerine through animal charcoal. The colourless glycerine is finally dehydrated in steam-heated vacuum pans.

Properties of glycerine.

Physical.

Glycerine is a thick, heavy and colourless liquid. It has no smell, but tastes sweet. It is very soluble in water, but insoluble in ether. It absorbs moisture.

Chemical.

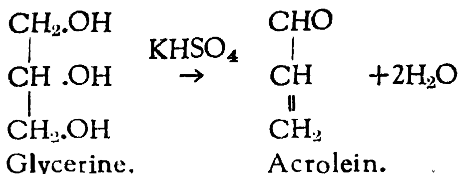
Glycerine is a trihydroxy alcohol, having a secondary alcoholic group. Acting as a secondary alcohol, it is able to reduce ammonical solution of silver nitrate to metallic silver.

Other reactions of glycerine.

(1) Make a cone of finely powdered $K_2Mn_2O_8$ and form a cavity at the apex of the cone. Pour into this cavity a little glycerine. The glycerine will catch fire in a short time.

(2) Take about 5 c. c. of glycerine and 1 gram of potassium hydrogen sulphate in a test tube. Heat it strongly. Glycerine is dehydrated and gives a characteristic irritating smell of an unsaturated aldehyde known as acrolein.

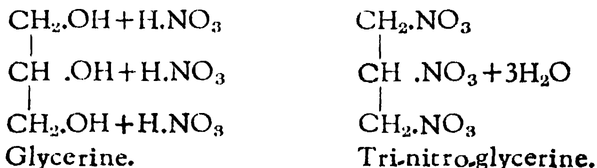
Reaction.



(3) Take 5% solution of borax. Make this solution pink, by adding to it a few drops of phenolphthalein solution. Add now to it, a little of about 15% glycerine solution. The *pink* colour is discharged, but re-appears on boiling. This is a very sensitive test of glycerine and is known as **Dunstan's test.**

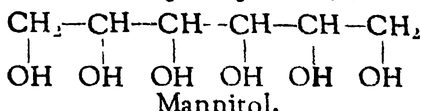
(4) Take a mixture of conc : HNO_3 and H_2SO_4. Allow glycerine to act on the mixture in a fine spray. The temperature of the mixture should never be raised to above 25°C. The glycerine is slowly esterified and the tri-nitro glycerine formed appears on the surface of the mixture as an yellow oily liquid.

Reaction.



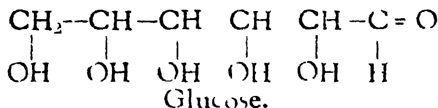
Note :—Conc : H_2SO_4 acts as a condensing reagent. Tri-nitro-glycerine is a violent explosive and is sensitive to shocks. Usually, it is detonated by the explosion from mercury fulminate. The use of tri-nitro-glycerine has been replaced by **dynamite**, which is a mixture of 70% of tri-nitro-glycerine and 30% of a porous sand called **kieselguhr.**

Hexa Hydroxy Alcohols



Mannitol.

Mannitol is closely related to sugar as glucose and fructose. **Glucose** is an oxidation product of mannitol.



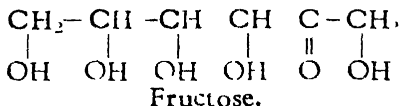
Glucose.

Note .—One of the primary alcoholic group —CH_2.OH of the mannitol is oxidised to aldehydic group —C=O.



Fructose is also an oxidation product of mannitol in which one of the secondary alcoholic group >C OH is oxidised to the ketonic group >C=O.





Fructose.

Carbohydrates.

Carbohydrates are compounds ***having carbon atoms*** associated with the atoms of hydrogen and oxygen in the proportion, in which they form water.

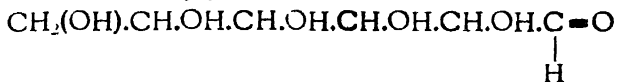
There are three classes of such carbohydrates.

1. Monosaccharides :—1. Glucose.
   2. Fructose.
2. Disaccharides :— Cane sugar.
3. Polysaccharides :— 1. Cellulose.
   2. Starch.

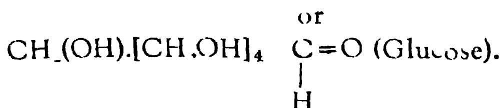
Monosaccharides.

Glucose or grape sugar :—$C_6H_{12}O_6$.

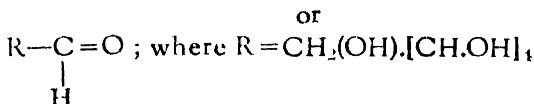
Constitution of glucose.



or



or



The various names, with which glucose is known.

1. Grape sugar : —Since; it is present in large quantities in grapes.

2. Dextrose . Since, its solution is able to rotate the plane of polarised light to the right (clock-wise).

3. Aldoses : - Since, it contains an aldehydic group C=O in its constitution and behaves in most cases, as an aldehyde.

Manufacture of glucose.

Glucose is obtained on a large scale by hydrolysing. starch with dilute mineral acids like HCl or H_2SO_4.

Properties of glucose.

Physical.

Glucose is a white crystalline substance, possessing sweet taste, very soluble in water, but in alcohol it is only sparingly soluble. *Its solution is optically active* and it is dextro.

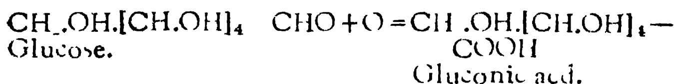
Chemical.

Since, constitutionally, glucose or aldose is represented as $R-\underset{\substack{|\\ H}}{C}=O$, where $R=CH_2OH.[CH.OH]_4$; it resembles an aldehyde in the following points :—

(1) It reduces Fehling's solution, to a red precipitate of cuprous oxide.

(2) It reduces ammonical solution of silver nitrate to metallic silver.

(3) It is readily oxidised to gluconic acid.

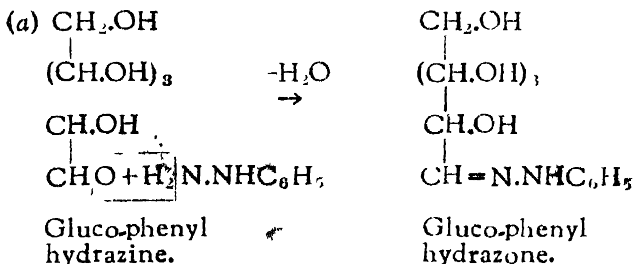


(4) It forms glucocyanhydrin with hydrocyanic acid.

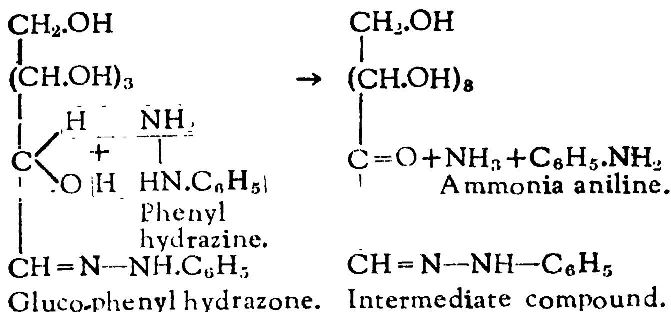
(5) It forms glucoaxime with hydroxyl amine.

(6) It reacts with hydrazine forming glucohydrazone.

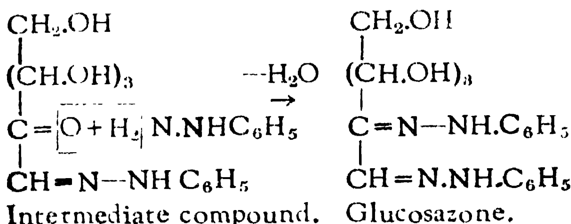
(7) It reacts with phenyl hydrazine in the following peculiar way : -

(*a*)


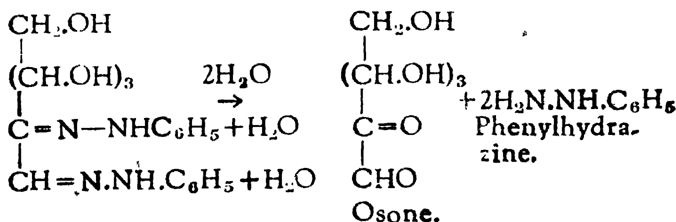
(*b*) The gluco-phenyl hydrazone reacts on the excess of phenyl hydrazine, forming an intermediate product along with ammonia and aniline.



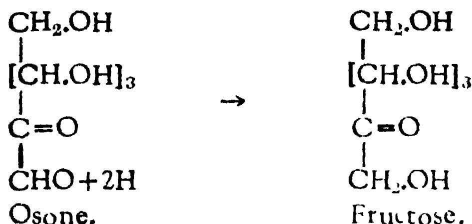
(*c*) The intermediate compound again acts on phenyl hydrazine, yielding **glucosazone.**



(*d*) The glucosazone on hydrolysis, is changed into **osone**, giving back phenylhydrazine.



(*e*) The osone, when reduced with zinc and acetic acid, is changed into *fructose*.



Notes :—(1) *Glucose*, undergoing the above series of chemical changes with phenylhydrazine is finally converted into *fructose*.

(2) *Glucose* does not form additive products with ammonia and sodium hydrogen sulphite, as an aldehydes does.

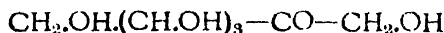
(3) Glucose does not give Schiff's test.

2. Fructose :—$C_6H_{12}O_6$.

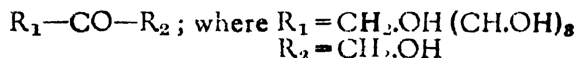
Constitution of fructose.



or



or



The various names, with which the fructose is known.

1. Fruit sugar:—Since, it is found in fruit juices.

2. Laevulose :—Since its solution is able to rotate the plane of polarised light to the left (anti-clockwise.

3. Ketoses :—Since, it contains a ketonic group >C=O, in its constitution and behaves in most cases as a ketone.

Manufacture of fructose.

Fructose is manufactured from inulin contained in the roots of *Jerusalem artichoke*, a species of sun-flower.

Properties of fructose.

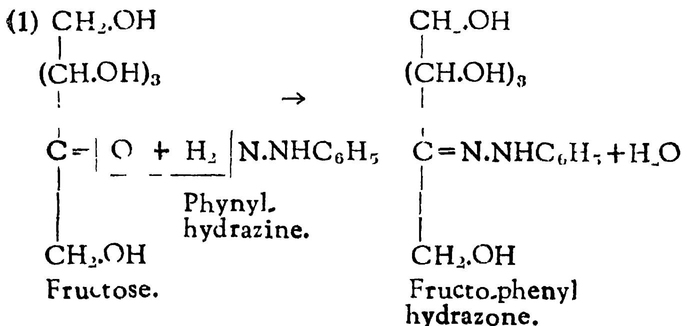
Physical.

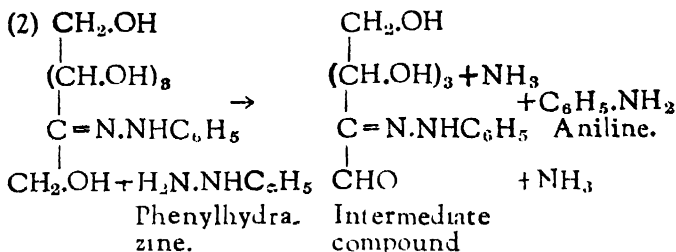
Fructose is a white crystalline substance, possessing sweet taste. It is readily soluble in water. *Its solution is optically active and is laevorotatory.*

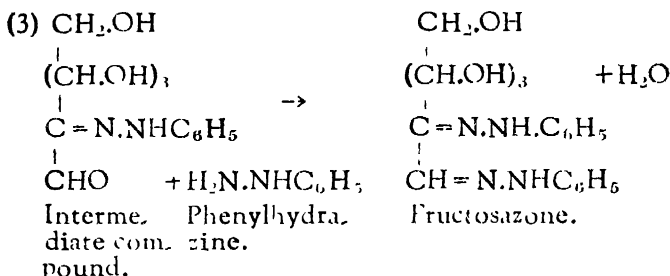
Chemical.

Since, fructose contains a ketonic group >C=O in addition to – OH groups, it behaves like a ketone as well as an alcohol. It behaves like glucose in its properties in much the same way, as an aldehyde resembles a ketone. Like glucose, fructose acts on hydroxyl amine, hydrocyanic acid and pheny-hydrazine.

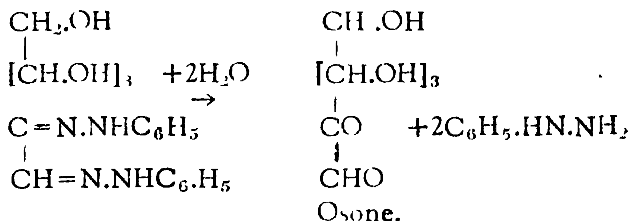
Reactions of fructose with phenylhydrazine.







The fructosazone on being hydrolised yields osone.



Note :—The phenylhydrazone of glucose is different from the phenylhydrazone of the fructose, but the osazone and subsequently osone of the both are identical. Fructose differs from glucose in points in which ketones differ from aldehydes. Fructose, however, reduces the ammonical solution of silver nitrate or Fehling's solution.

Disaccharides.

Cane Sugar :—$C_{12}H_{22}O_{11}$.

Cane sugar is a storage material of many plants and is mostly manufactured from sugar cane. The sugar cane is crushed under rollers. The juice, so extracted contains impurities, which are precipitated with lime. The impurities are filtered off and the juice is evaporated in vacuum pans. The concentrated juice is next allowed to crystallise in crystallising tanks. The sugar crystals are separated from molasses in centrifugal machines and the impurities are washed away with water spray.

Constitution of cane sugar.

The structrual formula of cane sugar is still uncertain. But it appears, that it has neither an aldehydic group nor a ketonic group.

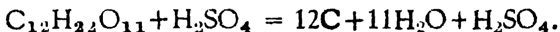
Properties of cane sugar

Physical.

Cane sugar is a white crystalline substance, ver. soluble in water. Its solution is optically active Cane sugar is dextrorotatory. It possesses a sweet taste. It melts at 160°C. When heated above this temperature, it forms a brown amorphous substance called caramel, which is used as a coluring matter for food staffs and wines.

Chemical.

(1) Cane sugar differs from glucose and fructose in getting charred, when treated with strong H_2SO_4.

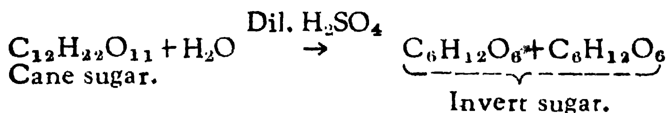


$$C_{12}H_{22}O_{11} + H_2SO_4 = 12C + 11H_2O + H_2SO_4.$$

(2) Unlike glucose and fructose, cane sugar is not a reducing agent nor it reacts with phenylhydrazine.

(3) Cane sugar is hydrolysed with dil. mineral acids into ***invert sugar***, which is a mixture of

glucose and fructose. The reaction is known as ***inversion.***



$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{\text{Dil. } H_2SO_4} \underbrace{C_6H_{12}O_6 + C_6H_{12}O_6}_{\text{Invert sugar.}}$$

Cane sugar.

The mixture of glucose and fructose so obtained is known as "Invert sugar", because, its solution is laevorotatory, whereas, the cane sugar is dextrorotatory. Since, fructose is more strongly laevo, the invert sugar could not be optically inactive, but it is laevorotatory.

(4) Since, the invert sugar contains glucose, cane sugar solution, after being treated with dilute mineral acids, is able to reduce Fehling's solution to a red precipitate of (Cu_2O) cuprous oxide.

(5) Strong nitric acid oxidises cane sugar to oxalic acid.

Polysaccharides.

1. Cellulose :—$C_6H_{10}O_5$.

Cellulose forms the main constituent of plant, fibres, paper and cotton.

Properties of cellulose.

Physical.

Pure cellulose is a colourless and transluscent fibrous substance. It is insoluble in water. It absorbs moisture from air. It is heavier than water. Wood is apparently lighter due to air spaces contained in the fibres.

Chemical.

(1) Cellulose turns brown, when it is heated.

(2) It decomposes before its melting point is reached.

(3) It gives acetic acid, acetone, wood tar, and methyl alcohol, when subjected to destructive distillation.

(4) Generally, it does not act on chemical reagents. Dilute soultion of acids and bases do not act on cellulose, as it is evident from the fact that filter-paper is not effected by various reagents.

(5) Strong caustic soda and potash act on cellulose and make it swell up as a gelatinous body. Cotton fibres, when treated with 20% caustic soda, take up a smooth glassy cylindrical appearance. This treatment of the fibres gives to them a peculiar silky lustre and the process is known as *mercerisation.*

(6) Strong H_2SO_4 acts on cellulose and changes it into carbonaceous matter. Dilute H_2SO_4 converts cellulose into a tougher and thicker substance. Paper treated with dilute H_2SO_4 is changed into parchment paper, which is water proof.

(7) Cellulose forms a soluble complex compound with cuperammonium hydroxide [$Cu(NH_3)_4(OH)_2$]. This soluble complex compound so formed, is used in the manufacture of artificial silk.

(8) Cellulose acts on nitric acid under different concentration and temperature, forming a higher (hexa-nitro) or a lower (tri-nitro) cellulose nitrate. We are familiar with a few of them.

(*a*) **Celluloid** :—It is a plastic solid formed by dissolving poorly nitrated cellulose along with some camphor in acetone. It is used in the manufacture of toys, combs, plugs, switches and other similar articles.

(*b*) **Collodian** :—It is a less nitrated cellulose, used in photography and is covering up wounds as a chemical skin.

(c) **Gun cotton** :—It is a highly nitrated cellulose, used as an explosive. Its solution in nitroglycerine mixed with a little of vaseline is used as a smokeless explosive called **cordite.**

(d) **Pyroxyline** :—It is a slightly less nitrated cellulose than gun cotton. Pyroxyline is largely used for the manufacture of cellulose paints.

2 Starch : – $C_6O_{10}H_5$.

Starch is a photosynthetic product, stored up in various forms in different parts of green plants, as a storage material. The most important sources of starch are potatos, wheat and rice.

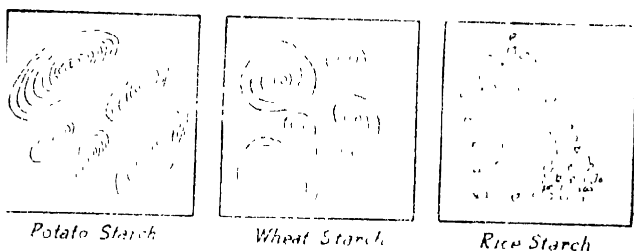


Fig. 47.

Properties of starch

Physical.

Starch grains have characreristic appearance as seen under a microscope. They are made up of concentric layers surrounding a nucleus. They, however, differ in shape and size, as obtained from different sources. Starch is insoluble in cold water. But at about 85°C, starch grains swell up in water and brust open, forming a colloidal solution, which sets to a jelly.

Chemical.

(1) Starch, heated to a low temperature is changed into dextrin, but, when heated to a high range of temperature, it gives the same products as we get, when wood is subjected to destructive distillation.

(2) Starch turns blue, when treated with free iodine. The colour is discharged by heating but reappears on cooling. It is a sensitive test for starch.

(3) Starch turns bright yellow, when treated with free bromine.

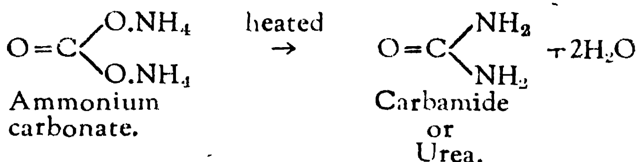
(4) Starch is hydrolysed by several *enzymes* differently.

1. Diastase converts it into maltose.
2. Ptyaline converts it into glucose.

Di-amides.

Carbamide or urea.

It is a di-amide related to ammonium carbonate.



$$O=C\begin{cases}O.NH_4\\O.NH_4\end{cases} \xrightarrow{\text{heated}} O=C\begin{cases}NH_2\\NH_2\end{cases} + 2H_2O$$

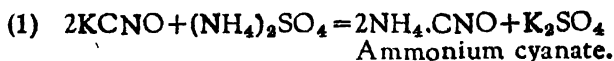
Ammonium carbonate. — Carbamide or Urea.

Urea is a vehicle for nitrogen excretion from animal bodies. It is present in sufficient quantity in animal urine, from which it was first obtained in 1773. In 1828 Wohler obtained urea by simply heating ammonium cyanate.

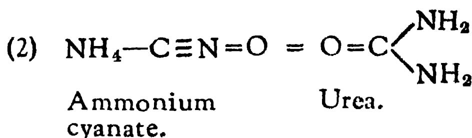
Preparation of urea.

It is prepared in the laboratory by heating a mixture of potassium cyanate and ammonium sulphate.

Reactions.



(1) $2KCNO+(NH_4)_2SO_4=2NH_4.CNO+K_2SO_4$
Ammonium cyanate.



(2) $NH_4—C\equiv N=O = O=C\begin{matrix}\diagup NH_2\\ \diagdown NH_2\end{matrix}$

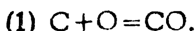
Ammonium cyanate. Urea.

Synthesis of urea.

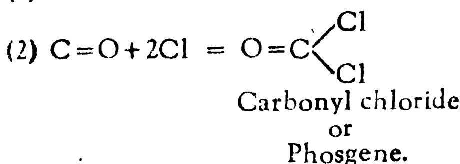
Is is synthesised from its elements in the following way :—

Carbon is burnt in a limited supply of air. The carbonmonoxide formed is treated with chlorine gas. The carbonmonoxide is changed into carbonyl chloride or phosgene; which, when treated with ammonia, is transformed into urea.

Reactions.

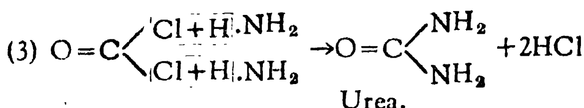


(1) $C+O=CO.$



(2) $C=O+2Cl = O=C\begin{matrix}\diagup Cl\\ \diagdown Cl\end{matrix}$

Carbonyl chloride
or
Phosgene.



(3) $O=C\begin{matrix}\diagup Cl+H.NH_2\\ \diagdown Cl+H.NH_2\end{matrix} \rightarrow O=C\begin{matrix}\diagup NH_2\\ \diagdown NH_2\end{matrix} +2HCl$

Urea.

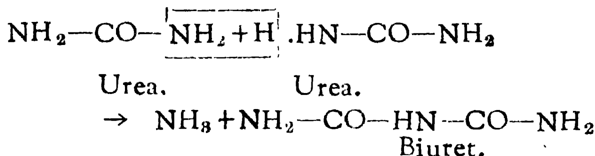
Properties of urea

Physical.

Urea is a colourless needle shaped crystalline solid, soluble in water and in alcohol, but insoluble in ether. It is almost colourless and has a saline taste.

Chemical.

(1) Urea, when heated strongly, is changed into buret.



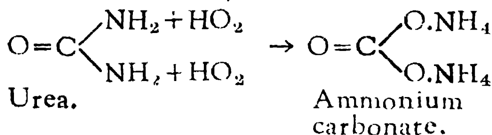
$$NH_2-CO-NH_2+H.HN-CO-NH_2$$

Urea. Urea.

$$\rightarrow NH_3+NH_2-CO-HN-CO-NH_2$$

Biuret.

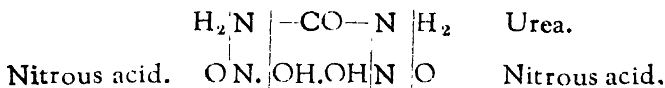
(2) Urea, on being hydrolysed is changed into ammonium carbonate.



$$O=C\begin{matrix}NH_2+HO_2\\NH_2+HO_2\end{matrix} \rightarrow O=C\begin{matrix}O.NH_4\\O.NH_4\end{matrix}$$

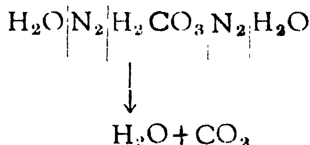
Urea. Ammonium carbonate.

(3) Urea, being treated with nitrous acid, is decomposed into carbondioxide, water and nitrogen.



H_2N | $-CO-N$ | H_2 Urea.

Nitrous acid. $ON.$ | $OH.OH$ | N | O Nitrous acid.

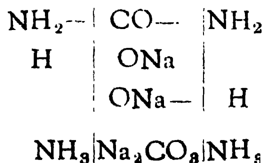


$$H_2O|N_2|H_2CO_3\,N_2|H_2O$$

$$\downarrow$$

$$H_2O+CO_2$$

(4) Urea, on being boiled with caustic soda, evolves ammonia and forms sodium carbonate.



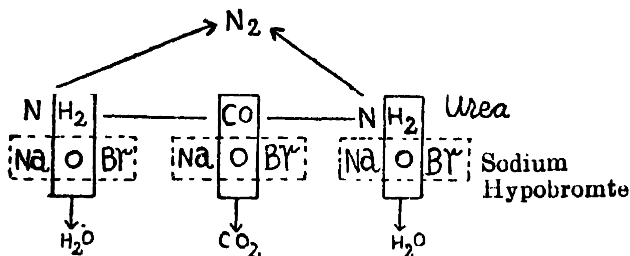
NH_2- | $CO-$ | NH_2

H | ONa |

| ONa$-$ | H

$$NH_3|Na_2CO_3|NH_3$$

(5) Urea, on being treated with sodium hypobromide, gives sodium bromide, water and evolves CO_2 and nitrogen.



Biuret test of urea.

Heat urea strongly in a test tube. The urea is changed into biuret. Dissolve it in a little water. Add to it a dilute solution of copper sulphate. Make the solution alkaline. A violet colouration is imparted to the solution.

Proteins.

Proteins are highly complex nitrogenous bodies, containing C, O, H, P, S and nitrogen. Such bodies are found in plant cells and also in secretions from certain organs of animals. They are colloidal in nature, on account of which, a systematic study of proteins could not be made and we know so little about them.

General characteristics of proteins.

(1) They are decomposed at a low range of temperature and are of high molecular weights.

(2) Being colloidal in nature, their particles in solution are electrically charged. They are positively charged in acid solutions, and negatively in the basic.

(3) Proteins are hydrolysed by strong HCl and certain enzymes into compounds of simpler molecules and ultimately, these compounds of lower molecular weights are decomposed into amino acids.

(4) Proteins dissolved in an alkaline medium, when treated with a dilute copper sulphate solution develops a violet colour (biuret test).

(5) Proteins give red colouration with Millions reagent.

Note :—Millions reagent is a solution of mercurous and mercuric nitrate in water, having free nitrous acid.

(6) Proteins, having sulphur in their constitution, when boiled with strong caustic soda and lead acetate, give a black precipitate. Non-sulphur protiens do not respond to this test.

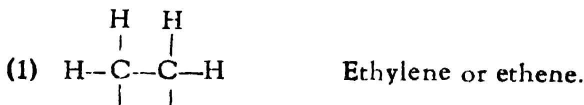
CHAPTER XI.

UNSATURATED HYDROCARBONS

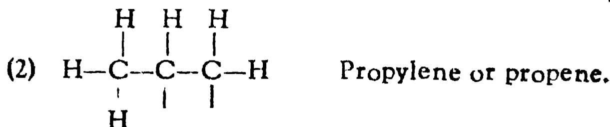
Refering to ethylene and acetylene mentioned on page 7, we know, that, there may be two classifications of unsaturated hydrocarbons.

1. *Ethylene or olifine series.*
2. *Acetylene series.*

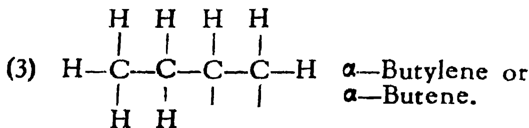
1. The hydrocarbons of **Ethylene** or **Olifine series** are those, in which, one of the four bonds of each of the two *adjacent* carbon atoms remain unsatisfied; as for example :—



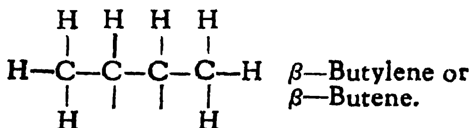
(1) Ethylene or ethene.



(2) Propylene or propene.



(3) α—Butylene or α—Butene.



β—Butylene or β—Butene.

In the constitution of these hydrocarbons ; the pair of unsaturated bonds can never remain free. Hence, they combine to form a **double linkage** between the two *adjacent* carbon atoms. The molecules of the members of **Ethylene series** are, hence, represented graphically as shown below :—

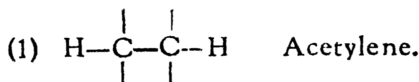
(1) $CH_2=CH_2$ Ethylene or ethene.

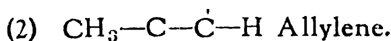
(2) $CH_3—CH=CH_2$ Propylene or propene.

(3) $CH_3—CH_2—CH=CH_2$ α—Butylene or α—Butene.

$CH_3—CH=CH—CH_3$ β Butylene or β- -Butene.

2. The hydrocarbons of **Acetylene series** are those, in which *two* of the four bonds of each of the two *adjacent* carbon atoms remain unsatisfied ; as for example :—





In the constitution of the molecule of these hydrocarbons, the two pairs of unsaturated bonds, never remain free ; but combine to form a **triple linkage** between the two *adjacent* carbon atoms. The molecules of the members of **Acetylene series** are, hence, represented graphically as shown below :—

(1) $CH\equiv CH$ Acetylene.

(2) $CH_3—C\equiv CH$ Allylene.

1. Ethylene Series.

Typical member.

Ethylene :—$CH_2 = CH_2$.

Preparation.

A mixture of ethyl alcohol and strong H_2SO_4 in the proportion by volume 1 : 2 is taken in a flask fitted up with a dropping fuunel D, containing some alcoholic mixture in the same proportion as that taken in the flask. The flask is heated over a sand bath to 160°C, till a regular stream of ethylene gas is evolved along with some ethyl alcohol vapour,

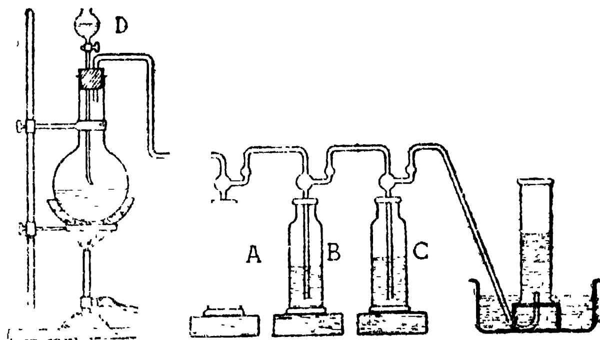


Fig. 48.

CO_2 and SO_2. To prevent frothing a little quantity of sand is also taken in the flask. As the evolution of the gas slackens, more of the alcoholic mixture is gradually introduced from the dropping funnel D, through its stem drawn out to a jet, which is slightly bent to prevent the escape of the ethylene gas up the dropping funnel. The impure ethylene gas passes through the wash bottles A, B and C, before it is collected by downward displacement of water as shown in Fig. 48. The alcohol vapour condenses in A and KOH solution contained in B and C absorbs CO_2 and SO_2.

Properties.

Physical.

Ethylene is a colourless gas, insoluble in water. It has a faint sweet smell. It acts as an anaesthetic.

Chemical.

(1) Ethylene burns in air with a smoky flame and in chlorine gas, it burns with a red flame.

(2) Ethylene enters into a number of reactions, forming *additive* products as noted :—

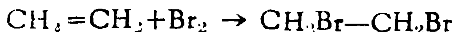
(*a*) In the presence of finely divided nickel, (acting as a catalyst) ethylene forms ethane (an additive product) with hydrogen.



$$CH_2=CH_2+2H \rightarrow CH_3-CH_3$$

Ethylene. Ethane.

(*b*) Ethylene forms additive products with chlorine, bromine and iodine, yielding dihalogen products.



$$CH_2=CH_2+Br_2 \rightarrow CH_2Br-CH_2Br$$

Ethylene dibromide.

Brown colouration of bromine water is discharged by passing ethylene gas through its solution. (*Distinction from saturated hydrocarbons*).

(*c*) Ethylene decolourises a pink solution of potassium permanganate. (*Distinction from saturated hydrocorbons*).

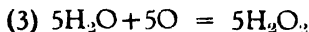
Reactions.



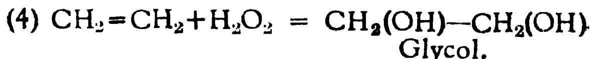
(1) $K_2Mn_2O_8 = K_2O+Mn_2O_7$



(2) $Mn_2O_7 = 2MnO+5O$

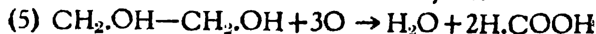


(3) $5H_2O+5O = 5H_2O_2$



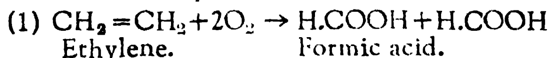
(4) $CH_2=CH_2+H_2O_2 = CH_2(OH)-CH_2(OH)$

Glycol.

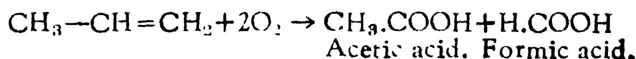


(5) $CH_2.OH-CH_2.OH+3O \rightarrow H_2O+2H.COOH$

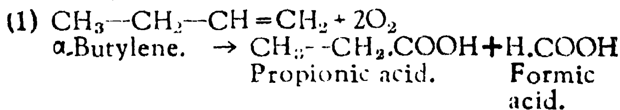
Note :—But on vigorous oxidation all compounds having double linkage between two adjacent carbon atoms are decomposed into two molecules of fatty acids. *The decomposition of such compounds take place only at the double linkage.* From the nature of the acids formed during the vigorous oxidation, the position of the double linkage in the molecule of higher homologues of ethylene series can be determined. For example :—

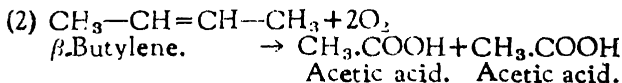


(2) Propylene on vigorous oxidation gives a mixture of acetic and formic acid.

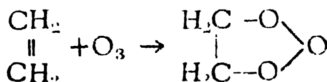


(3) α-Butylene on vigorous oxidation gives a mixture of propionic and formic acid, whereas, β-butylene gives only two molecules of acetic acid.

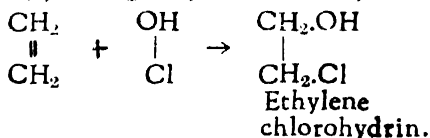




(*d*) Ethylene forms ethylene ozanide with ozone.

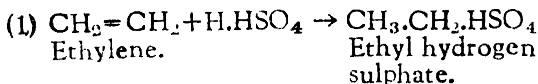


(*e*) Ethylene reacts with dilute hypochlorous acid solution, yielding ethylene chlorohydrin.

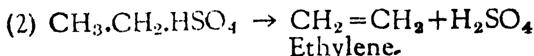


(*f*) Ethylene forms additive products with HCl, HBr, HCl and HCN as in (e).

(*g*) Ethylene acts readily with strong H_2SO_4 forming ethyl hydrogen sulphate, which, if heated gives out ethylene and H_2SO_4.



(1) $CH_2=CH_2+H.HSO_4 \rightarrow CH_3.CH_2.HSO_4$
Ethylene. Ethyl hydrogen sulphate.

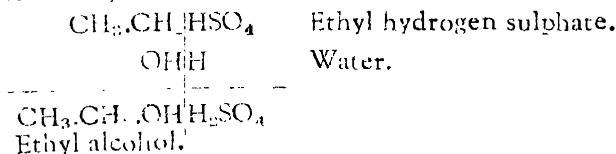


(2) $CH_3.CH_2.HSO_4 \rightarrow CH_2=CH_2+H_2SO_4$
Ethylene.

Note :—This reaction is helpful in purifying ethylene gas.

Again,

Ethyl hydrogen sulphate, when boiled with water, yields ethyl alcohol.



$CH_3.CH_2|HSO_4$ Ethyl hydrogen sulphate.
$OH|H$ Water.

$CH_3.CH_2.OH + H_2SO_4$
Ethyl alcohol.

Note :—This reaction is helpful in synthesising ethyl alcohol directly from ethylene.

From a number of reactions just studied, we have learnt that the compounds, having double linked carbon atoms readily form additive products with HCl, HBr, HI, HCN, HClO and H_2SO_4. In higher homologues of olefine series, the electro negative elements like Cl, Br, I or the radicals like CN, ClO and HSO_4, are always added to that doubly linked carbon atom, which has ***lesser number of hydrogen atoms***. For example :—

If propylene were to act on HCN, the cynogen group will go to the carbon atom having ***lesser*** number of hydrogen atoms.



$CH_3-CH=CH_2+HCN \rightarrow CH_3.CH(CN).CH_3$.

Uses of ethelyne.

(1) It is used in fruit preservation.

(2) It is used in the synthesis of a number of organic compounds.

(3) It is used in the manufacture of mustard gas.

(4) It is also used as an anaesthetic.

Note :—The members of ethylene series are also known as "*olefines*" since, ethylene dibromide, discovered in 1795 by four Dutch Chemists, is as an oil obtained from ethylene and hence, called "Olefant" or oil forming gas.

Baeyer's Strain Theory of double linkage.



JOHMN VON BAEYAR.

He is the founder of the Strain Theory.

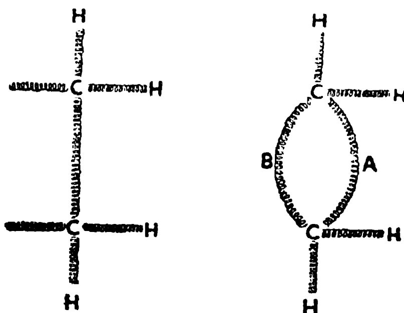
Unsaturated hydrocarbons, are chemically very active and the maximum reactivity of ethylene and other unsaturated hydrocarbons, is shown at the carbon atoms doubly linked. Baeyer, a German Chemist,

has accounted for the great chemical activity of the unsaturated hydrocarbons, as due to a kind of ***strain*** between the two carbon atoms doubly linked.

The evidence, detailed in the sterio-isomerism of tartaric acid, indicate that the four valencies of every carbon atom in the molecule of an organic compound, are distributed *in space* and are directed towards the angular points of a tetrahedron with a carbon atom at the centre. Baeyer advances his strain theory to explain the reactivity of the unsaturated hydrocarbons, by assuming, that each of the four bonds of a carbon atom behaves as a ***spring***. In an unsaturated compound like ethylene, the two unsatisfied *spring bonds* of the *adjacent* carbon atoms unite to form a double linkage under a ***strain***, as indicated by bulging out of the double bonds.

Since, the exact nature of distribution of valencies in space is difficult to draw, an attempt is made to give an idea of Baeyer's strain theory of double linkage by representing the structure of a molecule of ethylene with the help of a model sketch, in which, the four bonds of each of the carbon atoms are drawn as spring, all in *one plane*.

The model sketches of ethylene molecule.

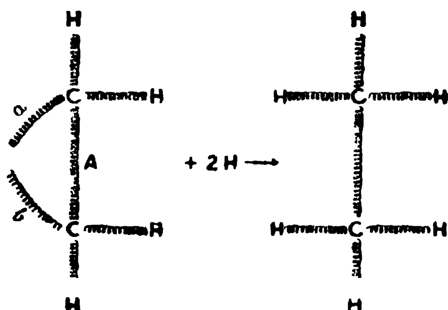


Model sketch No: I. Model sketch No: II.

Compounds, having free bonds, do not exist. Hence, the free *spring bonds* unite to form a single spring bond B, as shown in the model sketch No: II page 262, resulting in the displacement of the spring A, which consequeutly bulges out.

The two carbon atoms (in the model sketch No: II), of ethylene molecule has, thus, a double linkage under a strain.

Ethylene, however, when acts on two atoms of hydrogen, one of the double spring bonds B, readily breaks up into two halves "a" and "b", each combining with one atom of the hydrogen. The other spring bond A straightens up, releasing the strain of the double linkage. The unsaturated hydrocarbon is changed into saturated, as shown in the following model sketch No: III and IV.



Model sketch No: III. Ethylene.

Model sketch No: IV. Ethane.

2. Acetylene Series.

Typical member.

Acetylene :—CH≡CH.

Preparation of acetylene.

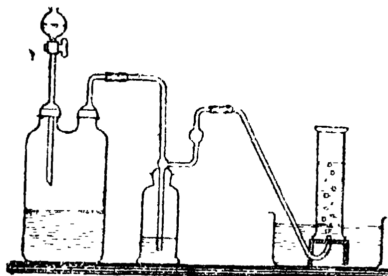
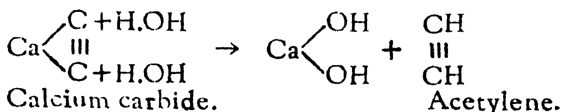


Fig. 49.

Acetylene is prepared by admitting water from a dropping funnel into a Woulf's bottle containing calcium carbide, which is hydrolysed, evolving acetylene, mixed with phosphine, ammonia and H_2S as impurities.

Reaction.



The impurities of the acetylene gas are removed by passing the gases through a wash bottle, containing a solution of cupric sulphate, as shown in Fig. No. 49. The gas is collected by the downward displacement of water.

Synthesis of acetylene.

Acetylene is synthetically obtained by passing a high voltage electrict current between two carbon

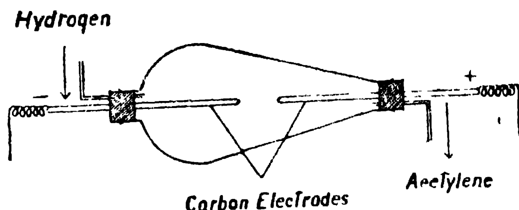


Fig. 50.

electrodes in a bulb, through the one end of which hydrogen gas is passed, as shown in Fig. No. 50. The acetylene gas comes out through the other end.

Properties.

Physical.

Acetylene is a colourless gas, smelling like garlic, when the gas is impure. It is slightly poisonous, It is easy to liquify the gas. Acetylene as a liquid is very explosive.

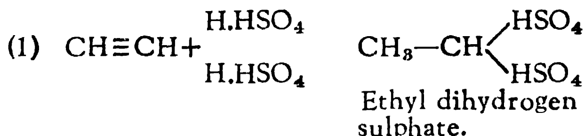
Chemical.

(1) Acetylene burns in air or oxygen with a bright flame. A flame produced from a jet of acetylene gas in a regulated supply of oxygen is known as oxy-acetylene flame, which is used in welding processes.

(2) Acetylene, on decomposition, liberates a large amount of heat energy and hence, it is an endo. thermic compound.

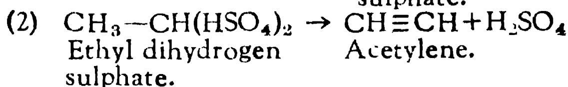
(3) Acetylene gives additive products with hydrogen, halogen, halogen acids and also hypochlorous acid, exactly as ethylene does.

(4) Acetylene combines with strong sulphuric acid, forming ethyl dihydrogen sulphate, which, on decomposition evolves acetylene.



(1) $CH \equiv CH + \begin{matrix} H.HSO_4 \\ H.HSO_4 \end{matrix}$ $CH_3-CH\begin{matrix} HSO_4 \\ HSO_4 \end{matrix}$

Ethyl dihydrogen sulphate.

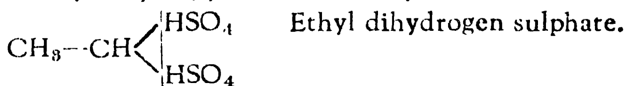


(2) $CH_3-CH(HSO_4)_2 \rightarrow CH \equiv CH + H_2SO_4$

Ethyl dihydrogen sulphate. Acetylene.

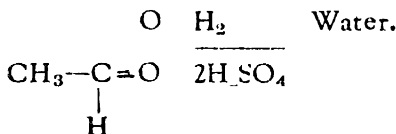
Note :—This reaction is used in purifying acetylene gas.

Again, ethyl dihydrogen sulphate so obtained, when hydrolysed, yields acetaldehyde.



$CH_3-CH\begin{matrix} HSO_4 \\ HSO_4 \end{matrix}$ Ethyl dihydrogen sulphate.

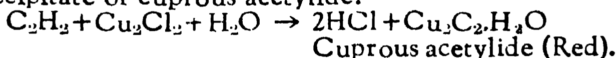
O H_2 Water.



$CH_3-\underset{\mid \atop H}{C}=O$ $2H_2SO_4$

Note :—The reaction is used in the synthesis of acetaldehyde and acetic acid. (Pages 138 and 139).

(5) When acetylene gas is passed into an ammonical solution of cuprous chloride, we get a red precipitate of cuprous acetylide.

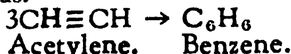


$C_2H_2 + Cu_2Cl_2 + H_2O \rightarrow 2HCl + Cu_2C_2.H_2O$

Cuprous acetylide (Red).

Note:—This reaction is used as a test for acetylene.

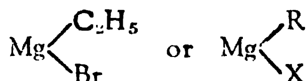
(6) When acetylene is passed through a red hot combustion tube, we get benzene, (the parent aromatic or closed chain hydrocarbon), as a condensation, product of the gas.



$3CH \equiv CH \rightarrow C_6H_6$

Acetylene. Benzene.

Grignard reagent or Organometallic Compound.



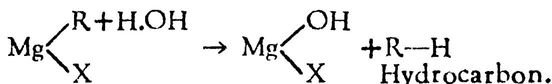
Preparation.

Take 2 grams of dry and clean magnesium powder in a flask fitted up with a reflux condenser. Introduce 20 c.c. of ether and about 3 c.c. of an alkyl halide. If there is no reaction, just warm it after 10 minutes waiting. As the reaction proceeds, the metal disappears after some times. On evaporating the solution, the Grignard reagent crystallises out along with ether. The composition of the crystalline Grignard reagent is $Mg.RX.2(C_2H_5)_2O$. The ethereal solution of the reagent is, however, used in all synthetical reactions. The ether does not seem taking part in the reactions.

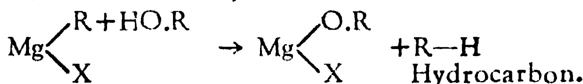
Synthetical uses of Grignard reagent.

(1) Synthesis of **hydrocarbons** from the reagent.

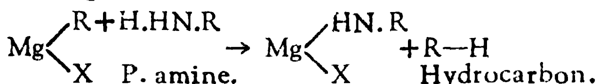
(*a*) *By hydrolysing the reagent.*

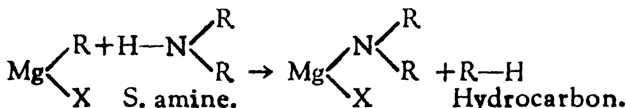


(*b*) *By the action of alcohol on the reagent.*



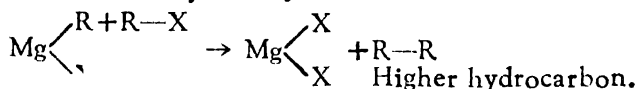
(*c*) *By the action of a primary or a secondary amine on the reagent.*





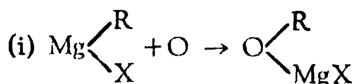
(2) Synthesis of **higher hydrocarbons** from the reagent.

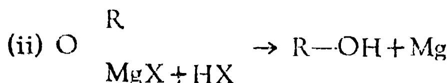
By the action of an alkyl halide.



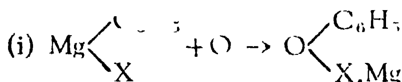
(3) Synthesis of **alcohols** and **phenols** from the reagent.

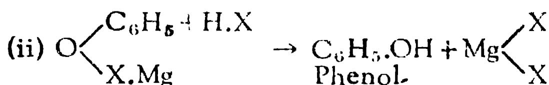
(*a*) *By the absorption of oxygen and subsequent treatment of the oxiginated product with a mineral acid we get a alcohol or a phenol.*





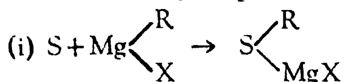
or,

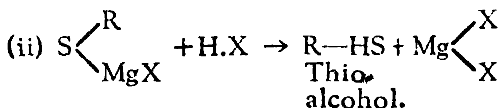




(4) Synthesis of **thio-alcohols** from the reagent.

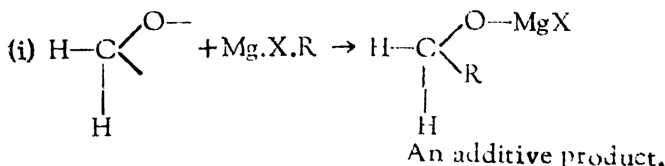
By the action of sulphur on the reagent.

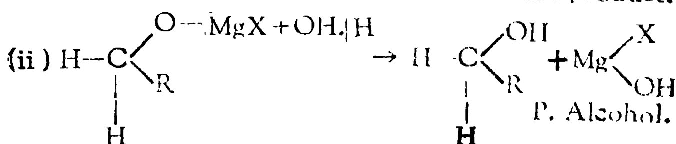




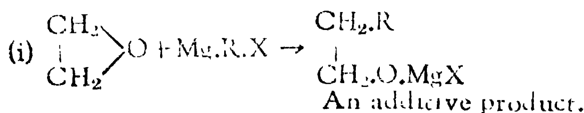
(5) Synthesis of a **primary alcohol** from the reagent.

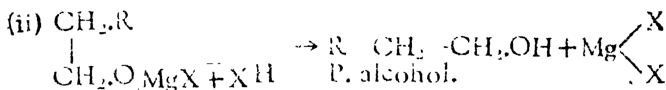
(*a*) *By the action of formaldehyde on the reagent.*
(Reactions proceeding in two stages).





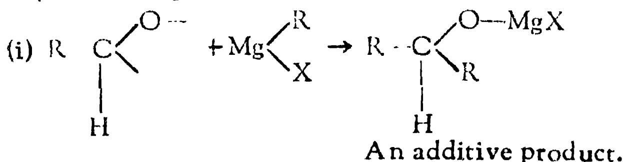
(*b*) *By the action of ethylene oxide on the reagent.*

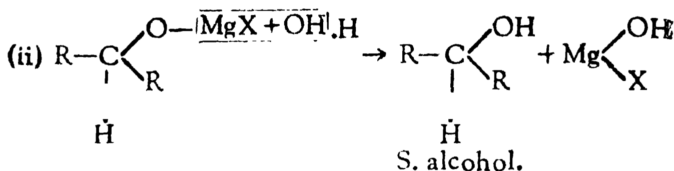




(6) Synthesis of a **secondary alcohol** from the reagent.

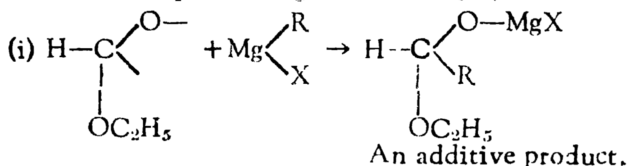
(*a*) *By the action of an aldehyde except formaldehyde.*
(Reactions proceeding in two stages.



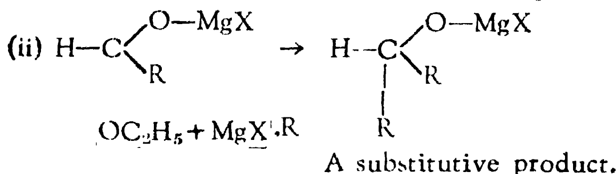


S. alcohol.

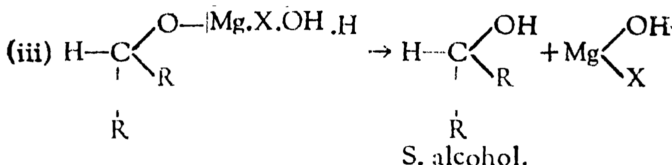
(b) By the action of ethyl formate on the reagent.
(Reactions proceeding in three stages).



An additive product.



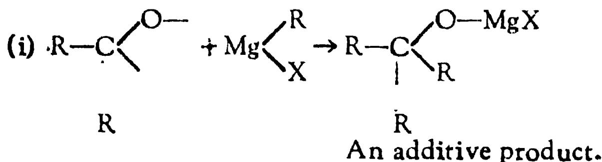
A substitutive product.



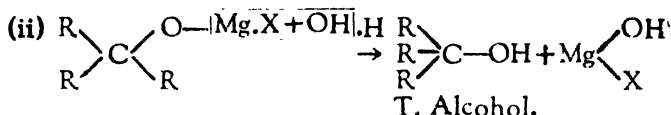
S. alcohol.

(7) Synthesis of a **tertiary alcohol** from the reagent.

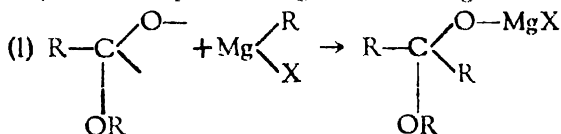
(a) By the action of a ketone on the reagent.
(Reactions proceeding in two stages).

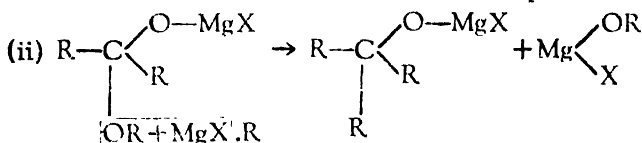


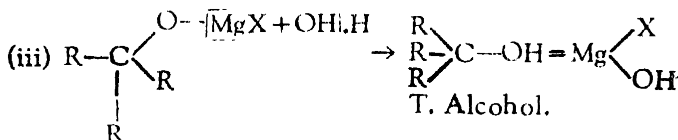
An additive product.



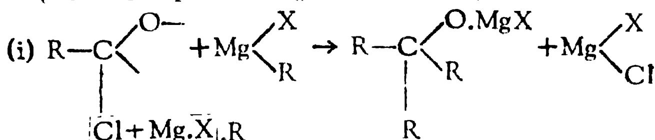
(*b*) *By the action of an ester of a fatty acid except a formate.*
(Reactions proceeding in three stages).

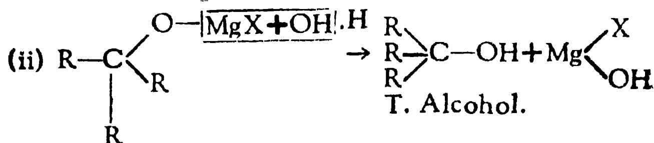






(*c*) *By the action of acid chloride on the reagent.*
(Reactions proceeding in two stages).

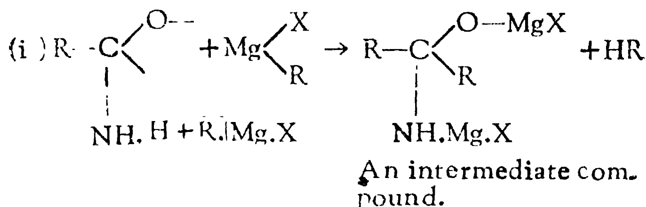




(8) Synthesis of a **ketone** from the reagent.

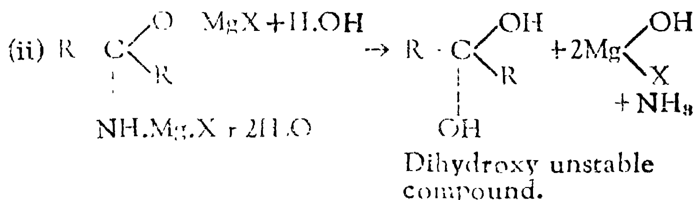
(*a*) *By the action of an amide on the reagent.*

(Reactions proceeding in three stages).

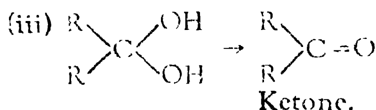


An intermediate compound.

The intermediate compound so obtained is hydrolised by three molecules of water, giving a dihydroxy unstable compound.



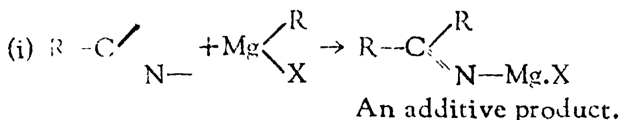
Dihydroxy unstable compound.



Ketone.

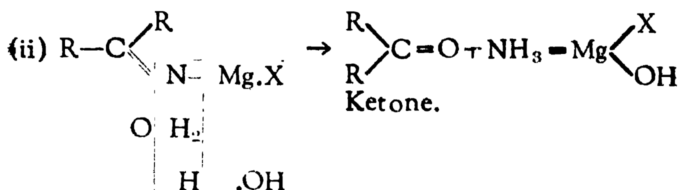
(*b*) *By the action of an alkyl cyanide on the reagent.*

(Reactions proceeding in two stages).



An additive product.

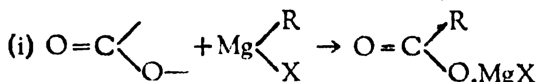
The additive product is hydrolised by two molecules of water and we get a ketone.

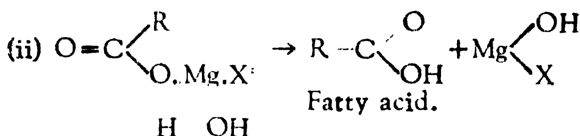


(9) Synthesis of a **carboxylic acid** from the reagent.

By the action of carbondioxide on the reagent.

(Reactions proceeding in two stages).

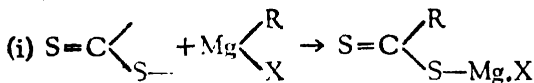


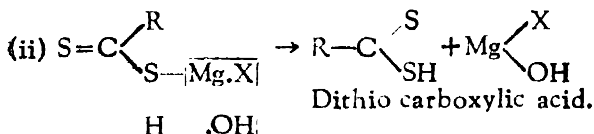


(10) Synthesis of **dithio carboxylic acid** from the reagent.

By the action of carbon disulphide on the reagent.

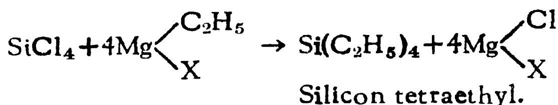
(Reactions proceeding in two stages).





(11) Synthesis of **silicon tetraethyl** from the reagent.

By the action of silicon tetrachloride on the reagent.

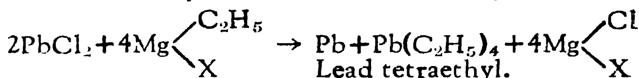


$$SiCl_4 + 4Mg\begin{matrix} C_2H_5 \\ X \end{matrix} \rightarrow Si(C_2H_5)_4 + 4Mg\begin{matrix} Cl \\ X \end{matrix}$$

Silicon tetraethyl.

(12) Synthesis of **lead tetraethyl** from the reagent.

By the action of lead chloride on the reagent.



$$2PbCl_2 + 4Mg\begin{matrix} C_2H_5 \\ X \end{matrix} \rightarrow Pb + Pb(C_2H_5)_4 + 4Mg\begin{matrix} Cl \\ X \end{matrix}$$

Lead tetraethyl.

Note :—Lead tetraethyl is used as a constituent in the anti-knock fuels, which burn smoothy under compression. The mixture of petrol vapour and air under high compression may explode pre-maturely of the motor cylinder before the piston head reaches the end of the cylinder, causing the engine a "knock". This causes a great loss to the engine power. Lead tetraethyl, when mixed with petrol, does not allow the fuel to explode prematurely. Hence, it is used as anti-knock in fuels.

CHAPTER XII.

CLOSED CHAIN OR AROMATIC COMPOUNDS.

The compounds, derived from the paraffin hydrocarbons are known as **aliphatic** or **open chain** compounds, whereas, those, derived from benzene are known as **aromatic** or **closed chain** compounds.

Benzene (C_6H_6) is the parent hydrocarbon and toluene (C_3H_8) is the second member of the family of the aromatic hydrocarbons. These two hydrocarbons are graphically represented, as already shown on page 8.

Benzene was discovered by Faraday in 1825, as a product of the destructive distillation of fats and vegetable oils. Later, it was prepared by the distillation of the gum benzoin with lime is the

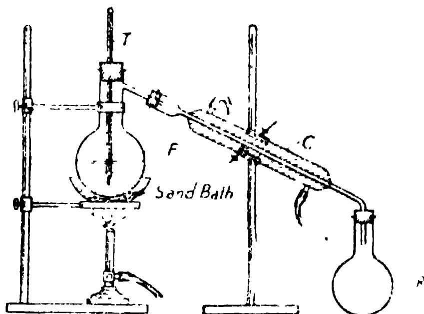


Fig. 51.

appatatus as shown in Fig. 51. At present, it is obtained on commercial scale by the fractional distillation of **coal tar,** which is one of the important products of destructive distillation of coal.

Manufacture of Benzene and Toluene.

Coal, on being subjected to destructive distillation, yields the following products :—

1. *Solids* :—Coke and gas carbon.

2. *Liquids* :—(1) Ammonical liquor and
(2) Coal tar.

3. *Gases* :—Coal gas.

The coal gas is next fractionally distilled and the following distillates are collected at different ranges of temperature :—

1. *Light Oil* :—Collected between 110°C and 120°C mostly containing (1) **benzene** and (2) **toluene.**

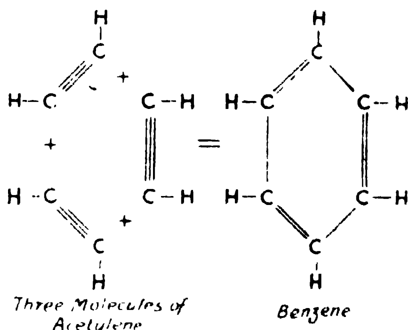
2. *Middle Oil* :—Collected between 120°C and 240°C mostly containing (1) **phenol** and (2) **Naphthalein.**

3. *Heavy Oil* :—Collected above 240°C containing amongst other compounds **anthracein.**

Thus, benzene and toluene are commercially obtained by the fractional distillation of the *light oil.*

Before entering into other evidences leading to the constitution of benzene, it would be desirable at present to accept **Kekules** hexagonal formula of benzene, as derived from Bertholot's synthesis of it, suggesting an alternate double linkage in the benzene ring of six carbon atoms as shown below :—

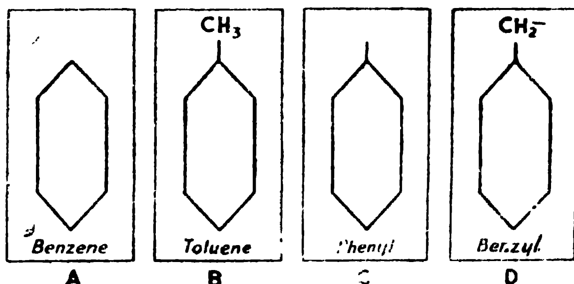
Bertholot's synthesis of benzene from acetylene led **Kekule** to suggest an alternate double linkage of the carbon atoms in the benzene ring.



Three Molecules of Acetylene *Benzene*

The simplified graphic representation of the benzene and toluene, along with their aryls, as adopted conventionally are given below :—

Note :—Aryls in the study of aromatic compounds are used for alkyls of the aliphatic series.



A = Benzene. B = Toluene.

C = Phenyl, which is the mono-valent aryl of benzene.

D = Benzyl, which is a mono-valent aryl of toluene—*the hydrogen atom dropping out from the side chain of the toluene.*

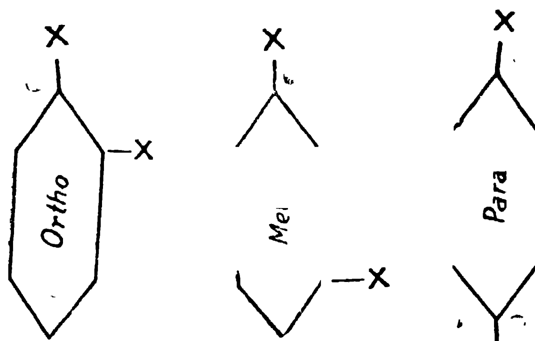
Some important conventional terms used in connection with the benzene ring.

(1) Each of the six carbon atoms of the benzene ring is termed **the caroon atom of the nucleus.**

(2) Each of the carbon atom attached to any of the six carbon atoms of the nucleus is known as **the carbon atom of the side chain.**

(3) The replacement of hydrogen atoms of the nucleus by other elements or groups is defined as **the chemical change at the nucleus**; whereas, when a hydrogen atom of the side chain is replaced by other element or group, the replacement is known as **the chemical change in the side chain.**

(4) The di-substitution products formed by the replacement of the two nuclear hydrogen atoms of the *adjacent* or *alternate* or *opposite* carbon atoms of the benzene ring, are respectively called, ortho, meta or para isomers of the compound, as shown below :—



Note:—The letter X has been used here to indicate any monovalent element or group in the nucleus.

Crum Brown and Gibson's Rule.

If a di-substitution product is derived from a mono substitution product of benzene, the position of the second substituent in its three isomers (ortho, meta and para) relative to the first say "X", can be predicted by *Crum Brown and Gibson's Rule,* according to which, if **HX** (the hydride of the mono-substituent) of the benzene ring is such, as can be **directly oxidised to HXO**; then, the disubstitution product will be the meta; otherwise a mixture of the ortho and para.

In other words, if the mono-substituent "X" in benzene is $-NO_2$, $-COOH$, $-CHO$, $-HSO_3$, $-CN$ or $-CO.R$, the di-substituent will occupy the meta position, but, if "X" is $-Cl$, $-Br$, $-I$, $-NH_2$, $-NHR$, $-NR_2$, $-OH$, $-CH_3$, the di-substituent will occupy ortho as well as para position.

General characteristics of benzene and other aromatic compounds.

(1) Aromatic compounds have a larger percentage of carbon atoms, than those of the aliphatic series have.

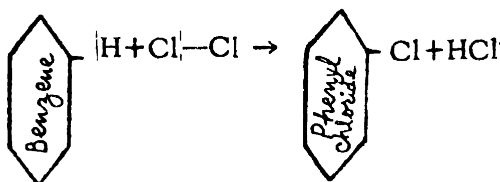
(2) Aromatic compounds, hence, burn with a smoky flame. *Aliphatic compounds generally burn with a non-smoky flame.*

(3) Benzene and other aromatic compounds have a very stable core of *six* carbon atoms. Under suitable experimental conditions, all such aromatic compounds, as have more than six carbon atoms, are converted into a compound having a stable core of six carbon atoms.

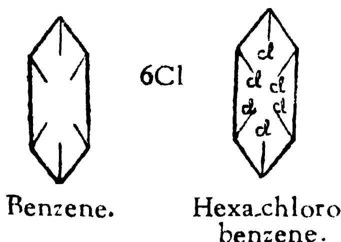
(4) *Chlorination or Bromination.*

The nuclear hydrogen atom of benzene is replaced by chlorine or bromine at ordinary temperature in the absence of light and the presence of a catalyst like, iron, aluminium, yielding substitution product.

Reaction.



Benzene also gives addititive products with chlorine or bromine in the direct sunlight without a catalyst.



Benzene. Hexa-chloro benzene.

Open chain saturated hydrocarbons *never* give additive products. (*Distinction from closed chain compounds*).

Notes :—(1) It can be experimentally shown that if every one of the six nuclear hydrogen atoms of benzene is replaced *in turn* by chlorine or bromine, all the six mono-chloro or bromo substitution products will be identical.

(2) The mono-chloro or bromo substitution product of toluene will be able to exist in four isomeric forms, namely ortho, meta and para and lastly benzene benzyl chloride or bromide, in which case substitution takes place in the *side chain.*

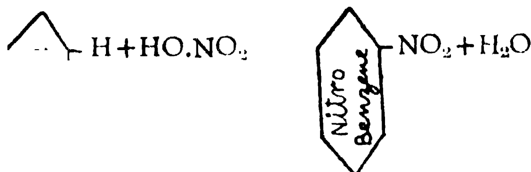
(3) In the absence of halogen carrier e.g. Fe or Al, if toluene is chlorinated or brominated at boiling temperature, the substitution takes place in the *side chain*.

(4) The di-chloro or di-bromo compound obtained from the mono derivative will be a mixture of the ortho and para variety (*Crum Brown and Gibson's Rule*).

(5) *Nitration.*

Strong nitric acid readily acts on the nuclear hydrogen atom of the ring, giving nitro-substitution product. The nuclear hydrogen atom combines with (OH) group of the nitric acid ($OH.NO_2$), forming water. The nitro group (NO_2) takes up the place of hydrogen in the nucleus.

Reaction.



Notes :—(1) The hydrogen atom attached to a carbon atom in an open chain compound *never* acts on nitric acid. (*Distinction from closed chain compounds*).

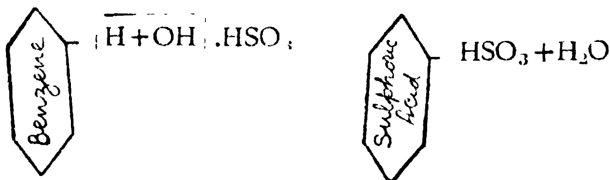
(2) The di-nitro compound, obtained from the mono-derivative, will be of the meta variety (*Crum Brown and Gibson's Rule*).

(3) Nitration takes place more readily in in the presence of strong sulphuric acid.

(6) *Sulphonation.*

Hot and strong sulphuric acid readily acts on the nuclear hydrogen atom of the ring, giving sulphonal substitution product (sulphonic acid). The nuclear hydrogen atom combining with (OH) group of the sulphuric acid ($OH.HSO_3$), forms water and the sulphonal group (HSO_3) takes up the place of the hydrogen atom in the nucleus.

Reaction.

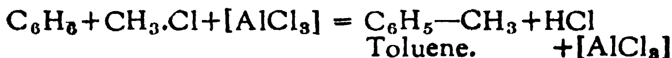


Notes :—(1) The hydrogen atom attached to the carbon atom of an open chain compound *never* acts on strong H_2SO_4. (*Distinction from closed chain compounds*).

(2) The di-sulphonal compound, derived from the mono derivative will be of the meta variety (*Crum Brown and Gibson's Rule*).

(7) *Friedal and Craft's Reaction.*

The nuclear hydrogen atom of the ring is replaced by an alkyl, when an alkyl halide reacts on a ring compound, in the presence of an anhydrous aluminium chloride, acting as a catalyst.



$$C_6H_6 + CH_3.Cl + [AlCl_3] = \underset{\text{Toluene.}}{C_6H_5—CH_3} + HCl + [AlCl_3]$$

Note :—This reaction is used in the preparation of the next higher member of benzene.

The behaviour of the halogen (chlorine, bromine or iodine) atom attached to the nucleus of the benzene ring.

1. The nuclear halogen atom is inactive towards reagents. It is not replaceable by —OH or —NH_2 group. The attachment of the halogen to the nucleus is firm. In the presence of a nitro group in the nucleus, the stability of the nuclear halogen is, however, weakened.

Note :—The chlorine atom of phenyl chloride $C_6H_5.Cl$ cannot be replaced by (OH) group by the action of aqueous solution of caustic soda or potash, nor, it can be replaced by ammino group, if phenyl chloride is treated with ammonia. But nitro-chloro benzene will act on aqueous solution of caustic soda, as well as on ammonia as indicated by the reactions noted below :—

$$(1)\quad C_6H_4\begin{cases}Cl\\NO_2\end{cases} + NaOH \rightarrow C_6H_4\begin{cases}OH\\NO_2\end{cases} + NaCl$$

Nitro-phenol.

$$(2)\quad C_6H_4\begin{cases}Cl\\NO_2\end{cases} + H.NH_2 \rightarrow C_6H_4\begin{cases}NH_2\\NO_2\end{cases} + HCl$$

Nitro-aniline.

Fittig's Reaction.

This is the only reaction, in which the nuclear halogen is replaced by an alkyl. When a mixture of chloro-benzene and methyl chloride is dissolved in dry ether and the solution is heated with metallic sodium, the nuclear halogen is replaced by an alkyl or an aryl.

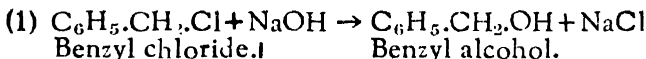
$$C_6H_5.Cl + CH_3.Cl + 2Na \rightarrow 2NaCl + C_6H_5—CH_3$$

Chloro-benzene. Methyl chloride. Toluene.

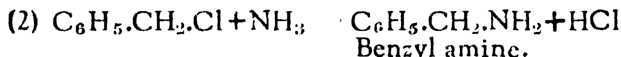
Notes :—(1) The halogen attached to the carbon atom of an open chain compounds is not stable and is, therefore, easily replaced by other groups like —OH and —NH_2 groups. (*Distinction from closed chain compounds.*)

(2) The halogen attached to the carbon atom in the *side chain* of an aromatic compound is replaceable by (OH) or (NH_2) group as in open chain compounds. Hence, benzyl chloride will act on aqueous caustic soda as well as on ammonia, yielding benzyl alcohol and benzyl amine respectively.

Reactions.



(1) $C_6H_5.CH_2.Cl + NaOH \rightarrow C_6H_5.CH_2.OH + NaCl$
Benzyl chloride. Benzyl alcohol.



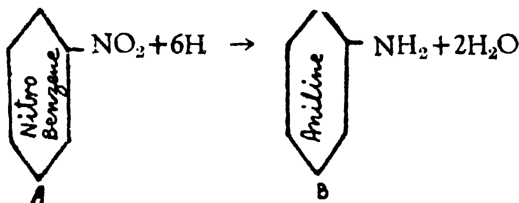
(2) $C_6H_5.CH_2.Cl + NH_3 \rightarrow C_6H_5.CH_2.NH_2 + HCl$
Benzyl amine.

The behaviour of the nitro group (NO_2) attached to the nucleus of the benzene ring.

(1) *The reduction of the (NO_2) group by a reducing agent in an acidic solution (zinc dust and HCl).*

The nitro group is reduced to amino group and the nitro compound is thus changed into aniline.

Reaction.



The reduction of the nitro-benzene to aniline is not so simple as indicated above. The reduction of nitro-benzene in an acidic solution proceeds in three stages. Nitro-benzene is first reduced to nitrosobenzene.

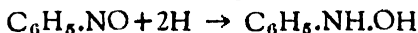
Reaction in the first stage.



$$C_6H_5.NO_2+2H \rightarrow C_6H_5.NO+H_2O$$

Nitrosobenzene is next reduced to phenyl hydroxylamine.

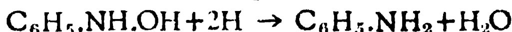
Reaction in the second stage.



$$C_6H_5.NO+2H \rightarrow C_6H_5.NH.OH$$

Finally phenyl hydroxylamine is reduced to aniline.

Reaction in the third stage.

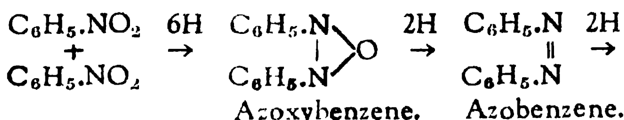


$$C_6H_5.NH.OH+2H \rightarrow C_6H_5.NH_2+H_2O$$

(2) *The reduction of the (NO_2) group by a reducing agent in an alkaline solution (zinc dust and caustic soda)*

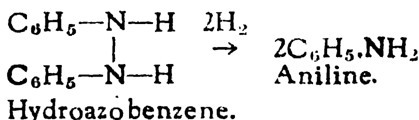
Two molecules of nitrobenzene are reduced together by six atoms of hydrogen, giving azoxybenzene, which on further reduction gives azobenzene and finally it is reduced to hydroazobenzene, which in its turn is reduced to two molecules of aniline.

Reactions.



$$\begin{matrix} C_6H_5.NO_2 \\ + \\ C_6H_5.NO_2 \end{matrix} \xrightarrow{6H} \begin{matrix} C_6H_5.N \\ | \\ C_6H_5.N \end{matrix}\!\!>O \xrightarrow{2H} \begin{matrix} C_6H_5.N \\ \| \\ C_6H_5.N \end{matrix} \xrightarrow{2H}$$

Azoxybenzene. Azobenzene.



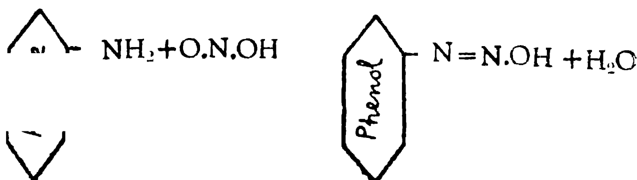
$$\begin{matrix} C_6H_5—N—H \\ | \\ C_6H_5—N—H \end{matrix} \xrightarrow{2H_2} 2C_6H_5.NH_2$$

Hydroazobenzene. Aniline.

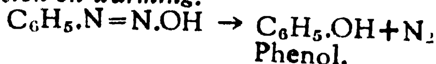
The behaviour of the amino group attached to the nucleus of the benzene ring.

(1) The nuclear amino group ($—NH_2$), when reacts with nitrous acid (OH.NO) **in cold**, is changed into diazonium hydroxyl group ($—N=N.OH$). The reaction is known as *diazotization*. The diazonium compound so formed **in cold**, being unsatble, is de. composed on warming and evolves nitrogen gas. The nuclear amino group is thus replaced by hyd. roxyl group (—OH) and the aniline is changed into phenol or carbolic acid.

Reaction in cold.



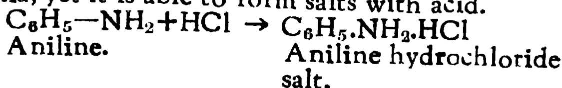
Reaction on warming.



$$C_6H_5.N=N.OH \rightarrow C_6H_5.OH+N_2$$

Phenol.

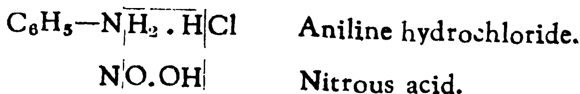
(2) The amino group ($—NH_2$) is less basic than ammonia, yet it is able to form salts with acid.



$$C_6H_5—NH_2+HCl \rightarrow C_6H_5.NH_2.HCl$$

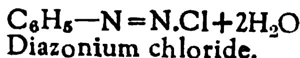
Aniline. — Aniline hydrochloride salt.

The aniline salts so obtained, when diazotized (*treated with nitrous acid in cold*) yields diazonium salts.



$C_6H_5—N|H_2 . H|Cl$ Aniline hydrochloride.

$N|O.OH|$ Nitrous acid.



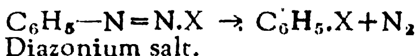
$$C_6H_5—N=N.Cl+2H_2O$$

Diazonium chloride.

The diazonium salts give the following three important reactions :—

(1) *Sandmeyer's Reaction.*

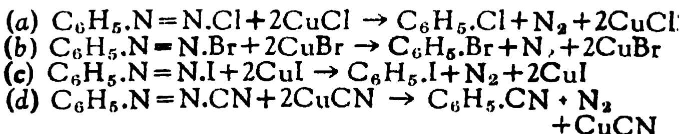
The diazonium salts, when warmed with ***a catalyst*** (an acidic concentrated solution of cuprous salts), are decomposed evolving nitrogen gas and yielding C_6H_5—X.



$$C_6H_5—N=N.X \rightarrow C_6H_5.X+N_2$$
Diazonium salt.

where X may be taken for Cl, or Br, or I, or CN. Phenyl chloride, bromide or iodide or cyanide can thus be prepared by warming diazonium chloride, bromide or iodide or cyanide with the corresponding cuprous salts.

Reactions.

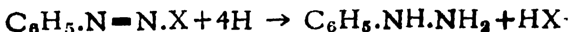


(*a*) $C_6H_5.N=N.Cl+2CuCl \rightarrow C_6H_5.Cl+N_2+2CuCl$
(*b*) $C_6H_5.N=N.Br+2CuBr \rightarrow C_6H_5.Br+N_2+2CuBr$
(*c*) $C_6H_5.N=N.I+2CuI \rightarrow C_6H_5.I+N_2+2CuI$
(*d*) $C_6H_5.N=N.CN+2CuCN \rightarrow C_6H_5.CN+N_2+CuCN$

Note :—Sandmeyer's reaction, thus, affords a convenient method of directly introducing halogen or cyano group in the nucleus of an aromatic compound. But, since, cyano group on hydrolysis is converted into —COOH and on reduction is charged into —$CH_2.NH_2$, Sandmeyer's reaction is also used in introducing —COOH or —$CH_2.NH_2$ group in the nucleus *indirectly*.

(2) Diazonium salt, when reduced with stannous chloride and hydrochloric acid, is changed into phenyl hydrazine.

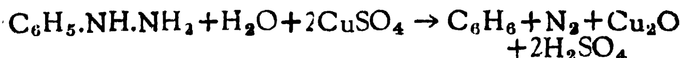
Reaction.



$$C_6H_5.N=N.X+4H \rightarrow C_6H_5.NH.NH_2+HX$$

The phenyl hydrazine so obtained is converted into benzene, when it is treated with a solution of copper sulphate.

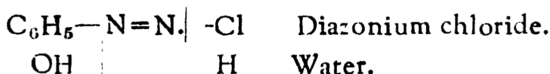
Reaction.



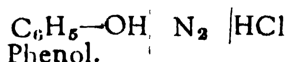
$$C_6H_5.NH.NH_2 + H_2O + 2CuSO_4 \rightarrow C_6H_6 + N_2 + Cu_2O + 2H_2SO_4$$

(3) *Hydrolysis.*

The diazonium chloride on hydrolysis, yields phenol, liberating nitrogen and hydrochloric acid.



$C_6H_5—N=N.$ | -Cl   Diazonium chloride.
OH   H   Water.



$C_6H_5—OH$ | N_2 | HCl
Phenol.

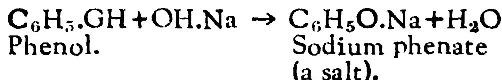
Notes :—(1) The amino group ($—NH_2$) attached to the carbon atom of the open chain compounds, does not give the reaction of *diazotisation* with nitrous acid. (*Distinction from closed chain compounds*).

(2) An alkyl amine is more basic than ammonia, but aniline is less basic. This indicates, that the alkyls like methyl and ethyl are *basic* or *electropositive* ; whereas, phenyl is *acidic* or *electronegative* group.

The behaviour of the hydroxyl group (—OH) attached to the nucleus of the benzene ring.

(1) The character of the nuclear hydroxyl group (—OH) is regarded acidic.

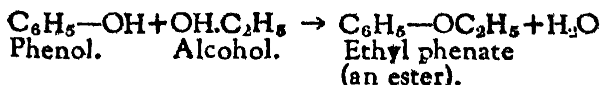
(2) The hydrogen atom of the nuclear (OH) group is replaced by Na or K, when the group reacts with an alkali. (*Neutralisation*).



$$C_6H_5.GH + OH.Na \rightarrow C_6H_5O.Na + H_2O$$

Phenol.   Sodium phenate (a salt).

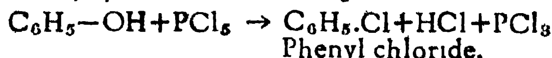
(3) The hydrogen atom of the nuclear (OH) group is replaced by an alkyl, when the group reacts with an alcohol. (*Esterification*).



$$C_6H_5—OH + OH.C_2H_5 \rightarrow C_6H_5—OC_2H_5 + H_2O$$

Phenol. Alcohol. Ethyl phenate (an ester).

(4) The nuclear hydroxyl group is replaced by chlorine, by the action of PCl_5.



$$C_6H_5—OH + PCl_5 \rightarrow C_6H_5.Cl + HCl + PCl_3$$

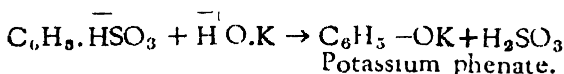
Phenyl chloride.

(5) The presence of the nuclear hydroxyl group, makes the rest of the benzene ring, much more chemically reactive.

The behaviour of sulphonic group (—HSO₃) attached to the nucleus of the benzene ring

(1) The character of sulphonic group ($—HSO_3$) is strongly acidic. The basicity of the acid depends on the number of sulphonic group in the nucleus.

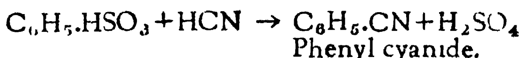
(2) The nuclea sulphonic group is replaced by (—OK) or (—ONa) group when treated with KOH or NaOH. The sulphonic acid is thus converted into potassium or sodium phenate.



$$C_6H_5.HSO_3 + HO.K \rightarrow C_6H_5—OK + H_2SO_3$$

Potassium phenate.

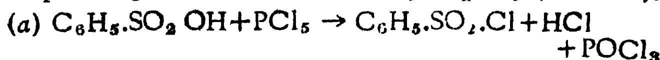
(3) The nuclear sulphonic group is replaced by cynogen group (—CN) when treated with hydro-cyanic acid.



$$C_6H_5.HSO_3 + HCN \rightarrow C_6H_5.CN + H_2SO_4$$

Phenyl cyanide.

(4) The sulphonyl group ($SO_2—OH$) is converted into ($SO_2.Cl$), ($—SO_2.NH_2$), ($—SO_2—OR$) by methods similar to those already studied in obtaining the corresponding derivatives of carboxylic group (—COOH).



(*a*) $C_6H_5.SO_2OH + PCl_5 \rightarrow C_6H_5.SO_2.Cl + HCl + POCl_3$



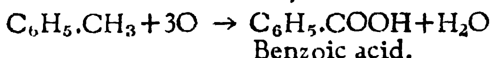
(*b*) $C_6H_5.SO_2.OH + H.NH_2 \rightarrow C_6H_5.SO_2.NH_2 + H_2O$



(*c*) $C_6H_5.SO_2.OH + OH.R \rightarrow C_6H_5.SO_2.OR + H_2O$

Behaviour of an alkyl group in the nucleus of benzene ring.

Any alkyl CH_3—, C_2H_5— or $CH_3.CH_2$— in the nucleus of benzene ring, when oxidised with chromic acid is converted into carboxylic acid.



$$C_6H_5.CH_3+3O \rightarrow C_6H_5.COOH+H_2O$$

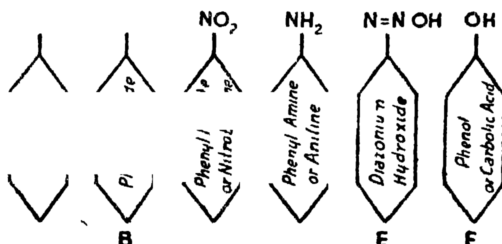
Benzoic acid.

Reactions in the side chain.

The behaviour of halogen (chlorine, bromine or iodine), the hydroxyl, the amino, the aldehydic and the carboxhlic groups in the **side chain** *are* **identical** *with those of the* **open chain** *compounds.*

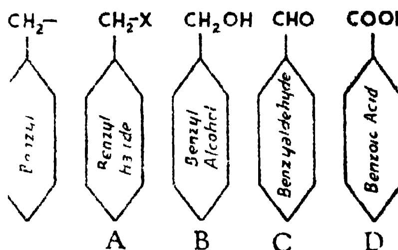
Relation of benzene to its derivatives

We have seen, that the *halogenation* of benzene nucleus, gives halogen substitution products. During *halogenation*, the halogen represented by X gets attached to the aryl called phenyl (A) and the phenyl halide is obtained as shown in B, below :—



Likewise, the *nitration* of benzene nucleus, gives nitro-substitution products. During *nitration*, the nitro-group is attached to the aryl called phenyl (A) and the nitro-benzene is obtained as shown in C above. The nitro-benzene, on being reduced with nascent hydrogen gives aniline as shown in D. The aniline yields diazonium compounds E and ultimately phenol F as shown above.

We have seen that by Fittig's reaction (page 283), phenyl chloride is changed into toluene. The side chain alkyl of the toluene is benzyl as noted below :—

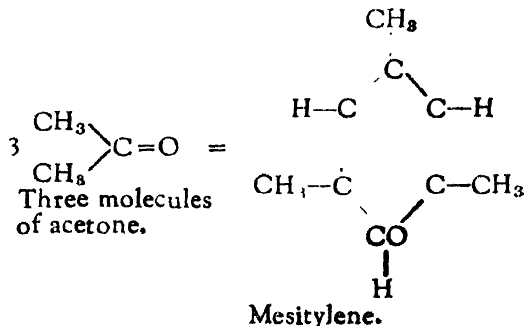


By introducing X (chlorine, bromine or iodine) to benzyl, we get phenyl halide A, which, when treated with NaOH (aqua), yields benzyl alcohol B. The benyl alcohol on oxidition gives benzyldehyde C, which on further oxidation is changed into benzoic acid D.

Conversion of open chain compounds into closed chain compounds.

(1) Bertholot's synthesis of benzene from acetylene. $3C_2H_2 \rightarrow C_6H_6$. (Read page 265)

(2) The synthesis of mesitylene, the fourth member of the closed chain hydrocarbon, by the condensation of three molecules of acetone.



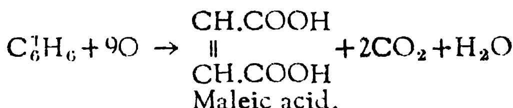
Mesitylene.

Conversion of closed chain compounds into open chain compounds.

(1) Benzene on being heated with $KClO_3$ and H_2SO_4 is changed into an open chain compound known as trichloroacetylacrylic acid, which is represented as $CCl_3.CO.CH{:}CH.COOH$.

(2) Benzene is directly oxidised to maleic acid by free oxygen in the presence of vanadium which acts as a catalyst.

Reaction.



$$C_6H_6 + 9O \rightarrow \begin{matrix} CH.COOH \\ \| \\ CH.COOH \end{matrix} + 2CO_2 + H_2O$$

Maleic acid.

Constitution of benzene.

Benzene, having the molecular formula C_6H_6 appears to be an unsaturated hydrocarbon, isomeric with dipropargyl, which is an important member of diacetylene series of the open chain compound. Its constitution is represented as below :—



$$CH_3.C \vdots C.C \vdots C.CH_3$$

The only other isomer of this compound has an ethylenic constitution as represented below :—



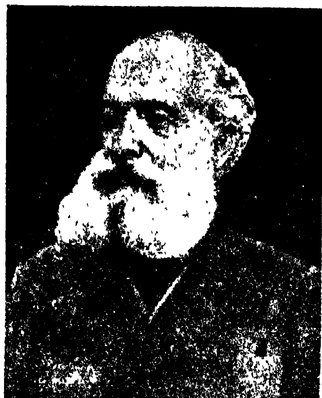
$$CH_2 : C : CH.CH : C : CH_2$$

Benzene differs from either isomers of dipropargyl in the following points :—

(1) Benzene gives additive products with chlorine or bromine only with difficulty, whereas, dipropargyl combines with halogen instantaneously.

(2) Benzene does not act on even strong oxidising agents like potassium dichromate.

Hence, constitutionly benzene cannot be an isomer of dipropargyl.



KEKULE.

Again, Kekule was led to conclude that benzene must contain a ring of six carbon atoms, each of which is comined with *one* hydrogen atom, on the consideration of the following important properties of benzene :—

(1) All the di-substitution products of benzene are known to occur in three isomeric forms—*ortho, meta and para*, in other words, known as *adjacent, alternate* and *opposite* respectively, thus, the behaviour of benzene is suggestive of its constitution as having the six carbon atoms connected in a ring with one hydrogen atom attached to each of the six carbon atoms.

(2) The six mono-substitution products of benzene, which may be obtained by replacing one by one, all the six hydrogen atoms from the benzene ring, are all identical. This behaviours of benzene clearly shows that ***the six hydrogen atoms of benzene are all chemically equivalent.***

But the position of the fourth valency of each of the six carbon atoms in the benzene ring remains unaccounted. In an attempt to account for the fourth valency Kekule suggested an alternative double linkage giving to benzene the following constitution :—





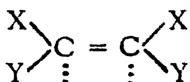
Ladenburg, however, pointed out that if this constitution be adopted, a di-substitution product of benzene should be able to exist in *four* forms ; but as already mentioned, experimental evidences show that the di-substitution product can exist in only *three* forms.

Kekule in an attempt to harmonise his formula, with the experimental facts, further suggested that the alternate single and double bonds in the constitution of benzene are rapidly oscillating. This modification was able to overcome the objection raised by Landenburg, but the fact, that in its chemical character, benzene is more a hydrocarbon of saturated series, than that of unsaturated one, did not lend supported to Kekule's idea of double linkage.

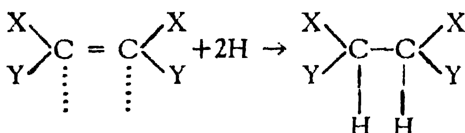
Amongst other several formulae Armstrong and Bamberger suggested the centric formula to explain the saturated character of benzene, but, this also has had points of weakness, and did not harmonise with the chemical properties of polynuclear ring compounds like naphthalein or anthracein.

Thiele in an attempt to explain the saturated nature of benzene ring, has advanced a hypothesis, according to which, the affinities of an ordinary double linkage is ***never fully utilized*** and always

leaves "residual valency". Thiel's idea of "residual valency" is illustrated in the formula noted below, where the dotted lines stands for the "residual valency" :—

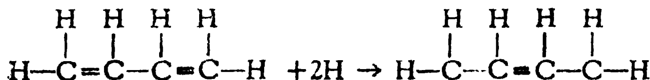


According to the views held by Thiele we know that, when an unsaturated compound yields an additive product, the "residual valencies" take up the work of full valency resulting in the disappearance of the double linkage as shown below :—



An additive product.

In a system of alternately single and doubly linkage, according to Thiele hypothesis the "residual valency" of the two central carbon atoms are mutually saturated and hence, addition, in such a system will *first* occur at the two carbon atoms at the extremes, as represented below :—

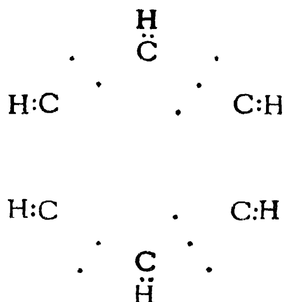


Such a system of alternate single and double linkage has been described by Tiele as "conjugated double bond".

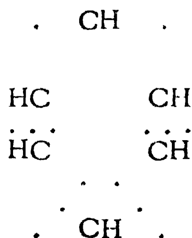
The above view, if extended to Kekule's ring formula, we can easily look upon benzene as a

closed system of "conjugated double bond", in which "residual vslencies" of the alternate *two central carbon atoms* are sufficiently satisfied.

This explain the saturated nature of benzene. In the light of electronic theory, the formula of benzene is shown as below :—



But the X-ray analysis of benzene, shows that the distances between each pair of carbon atom is 1·39°A. This length is smaller than that of a single bond and larger than rhat of a double bond in a compound of open chain series. J. J. Thomson suggested that each pair of carbon atoms is linked by three electrons as represented below :--



Thomson's electronic formula.

Such a consttiution of benzene is able to explain satisfactorily most of the experimental facts except the interpretations of atomic linkage in the light of wave mechines.

Orientation of Benzene Derivatives.

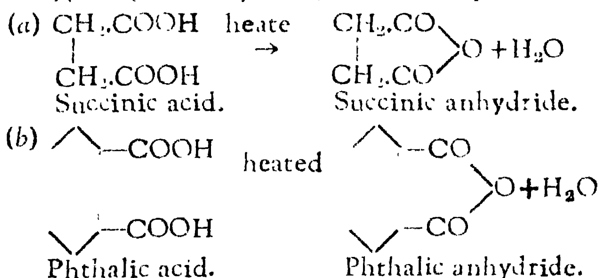
We know that the di-substitution products of benzene occur in three isomeric forms—ortho, meta and para. Orientation of these derivatives means the procedure to establish the constitution of the isomers.

There are two methods in use for the orientation of benzene derivatives :—

First method.

This method is based on the conversion of a given di-substitution product to be orientated into their corresponding di-carboxylic acids—*phthalic acid, isophthalic acid*, and *terephthalic acid*, whose constitution is already established as ortho, meta and para respectively.

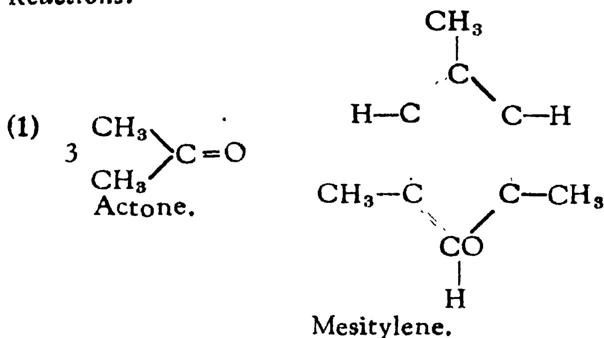
As a general rule, we know that a compound (aliphatic or aromatic) having two carboxylic groups (—COOH), attached to the two *adjacent* carbon atoms, are easily decomposed, on being strongly heated, giving its anhydride, as for examples :—



This behaviour of phthalic acid proves that in its constitution, the two carboxylic groups are attached to the nucleus of benzene in the ortho position. *The di-carboxylic acid of benzene, which on being heated gives its anhydride is thus orthophthalic acid.*

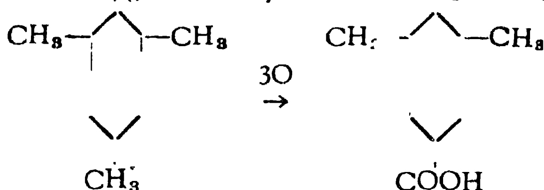
On the other hand, following the synthesis of isophthalic acid from acetone, it can be proved that the two carboxylic groups in its constitution, are attached to the benzene nucleus in the *meta position.*

Reactions.

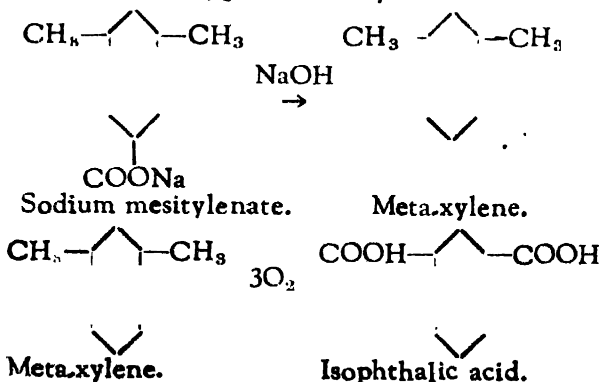


Mesitylene.

(2) Mesitylene (symmetrical trimethyl benzene) so synthesised, gives mesitylenic acid on oxidation.



(3) The sodium salt of mesitylenic acid on being treated with NaOH, gives meta-xylene.



Sodium mesitylenate. Meta-xylene.

Meta-xylene. Isophthalic acid.

The di-carboxylic acid of benzene, which is so synthetically obtained from acetone is isophthalic acid.

The constitution of the three isomeric forms of di-carboxylic acid of benzene, having been thus determined, the *terephthalic acid*, which is the third isomer, must be the *para compound.*

The constitution of these three isomers of di-carboxylic acid of benzene, being thus, established, they are used as standard in ascertaining the constitution of a given di-substitution product by adopting the following procedure :—

(1) The given di-substitution product of benzene in first converted into the corresponding di-chloro-halogen derivative, using suitable reactions step by step.

(2) Next, subjecting the di-halogen derivative to *Fittig's reaction*, both the halogen atoms in the nucleus are replaced by methyl groups.

(3) Finally, the di-methyl derivative, on being oxidised by chromic acid, is converted into the corresponding di-carboxylic acid.

If the di-carboxylic acid so obtained gives the properties of phthalic acid or isophthalic, the di-halogen derivative in question will be confirmed to be *ortho* or *meta* accordingly, otherwise, it is *para.*

Second method.

Körner's method used for establishing the constitution of any di-derivative of benzene, is based on further replacement of *one more* nuclear hydrogen atom by a similar or dis-similar group or of an atom. The number of isomers possible from the tri-substitution products, determines, whether the di-substitution product was ortho or meta or para. If the number of possible isomers of the tri-substitution product are two or three, the original di-substitution product must be ortho or meta respectively, whereas, if the tri-substitution product exists in *only one* form, the di-substitution product is *para.*

'omparison o Benzene and han

Tab

Benzene	han C_2H_6
1. It is a closed chai ompo	open compoun
2. It has a larger pe cen atoms. Hence, smoky flame.	on mo sma Hen me. mbe urns
3. It is a colourle q ng a characteristic sm	ou
4. It gives substitu s well as add tive products chlorine an bromine, under le experimei tal conditions. page 279].	on ib :utive produc lori d omine.

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No:

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5. It reacts readily with nitric acid, which gives ortho and para nitro-phenol. (Read page 28).	5. It is oxidised with nitric acid.
6. It reacts with strong sulphuric acid forming ortho and para phenol sulphonic acid. (Read page 282).	6. It acts on strong H_2SO_4. under three different experimental conditions. (Read page 75 and 76).
7. It is more acidic in reaction. (Read page 288).	7. It is alcoholic in reactions.
8. *Test.* Liebermann's nitroso reaction is used as a test for phenol. Phenol dissolved in conc : H_2SO_4, $NaNO_2$, along with a primary amine gives a dark coloured product, which when diluted with water gives a deep red colour changing to blue.	8. *Test.* Iodoform reaction is used as a test for alcohol.

Com on and E ami

.7.

Aniline :—$C_6H_5—NH_2$	**Ethyl amine :—$C_2H_5—NH_2$**
1. It is a closed chain compound.	1. It is an open chain compound.
2. It has a larger percentage of carbon atoms. Hence, it burns with a smoky flame.	2. It has a larger percentage of carbon atoms. Hence, it burns with a non-smoky flame.
3. It is a colurless liquid, but turns brown on account of the oxidation of thiophene, which is always present in aniline as an impurity.	3. It is a colourless gas above 19°C, smelling like ammonia.
4. It is a weaker base than ammonia. (Read page 288).	4. It is a stronger base than ammonia. (Read page 190).
5. It reacts with nitrous acid **in cold** forming diazonium compounds. (Read page 286).	5. It reacts with nitrous acid, which converts the ethyl amine into ethyl alcohol.
6. It is **readily** sulphonated forming ortho and para sulphanilic acid used as a drug.	6. It forms a salt with sulphuric acid.

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→ C_6H_5.l +HCl
Acetan

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4. Comparison of Benzaldehyde and Acetaldehyde.

Benzaldehyde ($C_6H_5.CHO$) resembles acetaldehyde in almost all the chemical reactions (described in table No: 10 and 11) **except** the following :—

1. Benzaldehyde ($C_6H_5.CHO$) does not reduce Fehling's solution.

2. Benzaldehyde gives hydrobenzamide with *dry* ammonia instead of benzaldo-ammonia.

$$3C_6H_5.CHO+2NH_3 = \underset{\text{Hydrobenzamide.}}{(C_6H_5.CH)_3N_2}+3H_2O$$

3. Benzaldehyde does not form resin with caustic soda. It resembles formaldehyde in giving *Cannizzaro's reaction* with NaOH or KOH.

$$\underset{\text{Benzaldehyd.}}{2C_6H_5.CHO}+OH.Na = \underset{\text{Benzyl alcohol.}}{C_6H_5.CH_2.OH}+\underset{\text{Sodium benzoate.}}{C_6H_5.COONa}$$

4. Benzaldehyde gives numerous *condensation* product.

5. Benzaldehyde is nitrated and sulphonated with strong HNO_3 and H_2SO_4 respectively, giving meta substitution products. (*Crum Brown and Gibson's Rule*).

6. **Test.**

Benzaldehyde smells strongly like bitter almond and its characteristic smell is takes as its convenient test.

HELPFUL QUESTIONS.

(Mostly from Examination Papers)

1. Write notes on (i) Isomerism, (ii) Intramolecular change, (iii) Substitution.

2. How is the methane prepared in the laboratory? What are the chief properties of this compound? "Methane is a saturated hydrocarbon". Explain this statement.

3. Write a note on the paraffin series of hydrocarbons giving their general formula, general methods of preparation, and chemical behaviour. What does the term "paraffin" signify?

4. What are kerosine oil, vaseline and glycerine? Write a short note on the kerosene oil industry.

5. Describe Wurtz's synthesis of the paraffin hydrocarbons. How, with the help of this reaction, may methane be converted into ethane?

6. How will you convert :

   (a) Methyl chloride into methane ;
   (b) Methane into methyl bromide ;
   (c) Propionic acid into ethane ;
   (d) Ethane into carbondioxide.

Give the structural formula of all the above compounds.

7. Describe any experiment you can perform to show the products of the destructive distillation of wood.

8. Describe a method for the manufacture of methyl alcohol.

9. What is the action of sulphuric acid on ethyl alcohol. Give the conditions, under which the various products are formed.

10. Give the methods for preparing (a) methyl alcohol, (b) methylated sprit, (c) ethyl alcohol and their principal properties.

11. Starting from methyl alcohol, explain, illustrating your answer by equations, how ethyl alcohol is produced.

12. What is the action of phosphorus trichloride on alcohol is general.

13, What reactions have led to the adoption of $CH_3.CH_2OH$ as the constitutional formula for ethyl alcohol ?

14. How is ethyl alcohol prepared on a large scale ? Mention the various raw materials used and state the changes involved in their conversion into ethyl alcohol.

15. What are the products obtained by the oxidation of ethyl alcohol ?

16. Explain clearly, what you understand by *fermentation.*

17. Write a note on *alcoholometry.*

18. Describe the preparation of a fairly pure specimen of acetaldehyde. By what tests will you identify a solution of acetaldehyde ?

19. Explain the action of formaldehyde on each of the following : (a) ammonical silver nitrate; (b) hydroxylamine, and (c) phenylhydrazine. Show, by means of complete structural formula, the relationship existing between formaldehyde, methyl alcohol and methane.

20. Give the chief chemical properties of methyl alcohol. How may it be distinguished from ethyl alcohol ? What different uses is methyl alcohol put to ?

21. What are the usual methods of preparing acetone in the laboratory ? How is it manufactured industrially ? Compare and contrast the properties of acetone and acetaldehyde.

22. How is pure acetaldehyde prepared ? Described its properties, giving a sketch of the apparatus. Give equations.

23. By what different methods may formaldehyde be synthesised ? How does it react on (i) hydgen cyanide, (ii) sodium bilsulphite, (iii) phenyl hydrazine, (iv) phosphorus pentachloride, and (v) sodium hydroxide ? Give equations, and name the products obtained in every case.

24. How is acetaldehyde prepared from ethyl alcohol ? How does the structural formula given to it accounts for its properties ? Illustrate your answer with examples.

25. How are formaldehyde and acetone prepared ? Compare and contrast the behaviour of an aldehyde and a ketone.

26. Describe a method for the preparation of an aqueous solution of formaldehyde. State it important properties, giving equations.

27. Suppose you are given four liquids and told that amongst them are :—Methyl alcohol, ethyl alcohol, acetone and formalin. How would you proceed to discover, which was which ?

28. Give general methods of formation and important reactions, of fatty acids. How would you convert a fatty acid into (a) a paraffin, (b) an aldehyde, and (c) a ketone ?

29. How can a pure, anhydrous sample of formic acid be prepared in the laboratory? In what important respects, does it differ from acetic acid?

30. Describe a method for preparing formic acid, and compare its properties with those of acetic acid?

31. How is ordinary vinegar manufactured? How would you prepare from it (a) glacial acetic acid, (b) marsh gas, and (c) acetone?

32. How would you obtain:

(a) Acetamide from acetic acid;
(b) Methyl alcohol from methylamine;
(c) Methylamine from acetamide;

Give all necessary equations.

33. Compare the properties of fats and soaps, and show how you will distinguish them experimentally.

34. How is methylamine prepared? Compare its properties with that of ammonia. Show the structural relationship between these compounds?

35. What are the differences between an amine and an amide? How will you distinguish one from the other? How an acetamide is converted into methylamine?

36. Describe all the points you know, in which, oxalic acid and tartaric acid resemble and differ.

37. Compare in a tabular form the properties of urea with those of acetamide. By what tests can these compounds be distinguished from each other?

38. How may glycerol be synthesized?

39. How is acetyl chlotide acted upon by each of the following substances:—(1) water, (2) ethyl alcohol, (3) ammonia, (4) sodium acetate? Give equations.

40. What is the action of a boiling solution of caustic soda on the following substances :—(a) acetaldehyde, (b) acetamide, (c) chloroform, and (d) fats.

41. Compare and contrast the physical and chemical properties of ethyl alcohol, glycerol and phenol.

42. How would you prepare acetyl chloride? Draw a neat sketch of the apparatus you will use and give by means of equations the action of water, ethyl alcohol, and ammonia on acetyl chloride.

43. What is soap? Can soap be prepared from kerosene oil? Describe briefly the manufacture of soap.

44. Give the methods of preparation and properties of ethers. Why do you present diethyl ether as $C_2H_5.O.C_2H_5$?

45. Describe, with all essential details, along with the sketch of the apparatus used, the preparation of ethyl ether. How would you purify and make it anhydrous?

46. How is aniline related to benzene? How may it be obtained from benzene. Give important tests and uses of aniline.

47. Write all you know about aniline.

48. Make a comparision between methylamine and aliline as regards their properties.

49. Give the important points of distinction between the aliphatic and the aromatic compounds.

50. What do you understand by the terms—(a) carbohydrate; (b) monosaccharide; (c) aldose; (d) fermentation; and (e) inversion?

51. What simple tests would you carry out to show that (i) *Gur* (from sugar-cane juice) contains both can sugar and grape sugar; (ii) What contains starch; (iii) "tincture iodine" contains ethyl alcohol?

52. Describe the preparation of ethyl bromide in the laboratory, giving a neat sketch of the apparatus. Give the various important synthetical reactions of this compound.

53. Describe two different reactions by which it is possible to *go up* the series. By what reactions may methyl alcohol be converted into ethyl alcohol and vise versa ?

54. From what source is phenol obtained ? Compare the properties of phenol and ethyl alcohol.

55. Give equations to present the following reactions :—

Action of ammonical silver nitrate on glucose ;

Action of phenylhydrazine on glucose ;

Action of hot, concentrated hydrochloric acid on cane sugar.

56. Describe, with experimental details, how chloroform is prepared, givining a sketch of the apparatus used. What are its important properties ?

57. Explain the meaning of the following terms : (a) additive product ; (b) double bond ; (c) triple bond ; (d) polymerization, and condensation.

58. Compare the properties of ethylene and acetylene. How are they prepared and synthesised.